Solicitation: Particle Matter Supersites Program, U.S. Environmental Protection Agency

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Title: St. Louis-Midwest Supersite

Investigators and Institutions

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Project Period: January 1, 2000 through December 31, 2003

Project Cost: $ 3,883,566

Project Summary

A fine particulate matter Supersite is proposed in Metropolitan St. Louis (IL-MO), a major industrial and population center. This comprehensive research program will provide physical and chemical measurements needed by the health effects, atmospheric science and regulatory communities, in a setting broadly representative of the urban Midwest. The proposal is submitted by a public/private partnership that provides significant leveraging of resources.

Measurements will be fully integrated with three large health effects programs: the EPA/Harvard Center on Ambient Particle Health Effects, the NIEHS/Harvard Program Project on Ambient Particles Cardiac Vulnerability, and the EPRI Particle Exposure Assessment Program. These health studies will: (i) investigate relationships between personal exposures and outdoor concentrations, and examine the health effects of chronic exposures; (ii) identify biological mechanisms responsible for particle health effects; (iii) identify susceptible populations; and (iv) investigate the relative toxicity of the different particle constituents.

The measurement strategy features sustained sampling using state-of-the-art continuous monitoring techniques for particle mass, size and composition. The high time resolution of the data will permit novel hypotheses and interpretive techniques to be tested in both source apportionment and health effects studies. Measurements will be conducted throughout a full year at the core site, located in an urban residential neighborhood of St. Louis City, providing context for episodes and to support the time series epidemiological studies. A movable instrument platform will rotate between four satellite sites in the greater St. Louis region, collecting 21-24 successive days of measurements at each site during each season. The satellite sites will be used to examine the impacts of local sources and to investigate the spatial patterns of outdoor exposures. Emphasis in designing the measurement platforms has been placed on identifying advanced methods with demonstrated or potential ability to operate reliably for extended periods with limited attendance.

In situ measurements will obtain temporally resolved data for particle size, mass, nitrate, sulfate, organic and elemental carbon, and five metals of environmental significance. Instrumentation newly developed at the University of Minnesota will continuously measure particle size distributions as well as integral moments of the particle size distribution (range 3 nm – 10 μm). The latter method shows promise as a cost-effective approach for obtaining particle size data for health effects studies, and will be validated using conventional particle sizing techniques. Continuous instruments developed by Harvard University for particle mass, nitrate and sulfate will be deployed at both the core and satellite sites to provide data for health effects studies and assessing temporal and spatial variability. A semi-continuous carbon analyzer will be used at the core site to obtain hourly average elemental and organic carbon concentrations. A novel semi-continuous elemental analysis system developed by the University of Maryland will be operated at the core site to provide hourly-average data for five heavy metals of significant interest to the health effects and source apportionment communities. The experience to be gained through the field testing of these advanced monitoring techniques will be shared with the scientific and instrument manufacturing communities.

Substrate methods will be used for 24-hour integrated measurements of particle mass and composition. These measurements will feature enhancements to the chemical speciation network methods and will be used to: (a) evaluate the continuous monitoring techniques; and (b) provide detailed chemical characterization of particles beyond the baseline analyses for the chemical speciation network (precursor gases, particle acidity, an expanded suite of particulate ions, and water soluble metals). Elemental analysis strategies are emphasized because of their importance to health effects and source apportionment studies. Collocated samples will be used to compare four distinct analytical methods - XRF, ICPMS, INAA and GFAA. Based on the results, one method will be chosen to analyze the full year of daily samples for both the core and satellite sites. 24-hour integrated measurements at both sites will provide data to: (a) evaluate the performance of the continuous monitors in various environments; (b) investigate temporal and spatial variations in particle mass and composition; and (c) support the health effects studies.

Samples will also be collected for retrospective analysis of trace element and organic compound composition. About 500 one-hour integrated samples will be analyzed for twelve trace elements in addition to the sustained hourly-average measurements for five elements. Detailed organic speciation will be performed for more than 100 of the 24-hour integrated samples. These analyses will provide data to support both health effects and source apportionment studies.

A consortium of six universities from across the country has been assembled to undertake the proposed St. Louis Supersite program. The investigators include experts in methods development, particle chemistry and physics, field studies, data processing and analysis, source apportionment, exposure assessment, and quality assurance. The Principal Investigator – Dr. Jay Turner of Washington University – will work closely with the Executive Management Team consisting of Dr. Judith Chow (Desert Research Institute), Dr. Petros Koutrakis (Harvard University), Dr. Peter McMurry (University of Minnesota) and Dr. Warren White (Washington University) to guarantee successful execution of this project.

This proposed project runs from January 2000 through December 2003. First year activities focus on study planning and design with measurements phased in during the 4th Quarter. Sustained monitoring with the full suite of measurements will be conducted from January 1, 2001, through December 31, 2001. The two remaining years will be used for chemical characterization, data analysis and reporting.

D. PROJECT DESCRIPTION

D.1. OBJECTIVES AND PROPOSAL OVERVIEW

The overall goal of the proposed Supersite is to provide the physical and chemical measurements needed by the health effects community, the atmospheric science community and the regulatory community to properly assess the impact of particulate matter exposure on human health and to develop control strategies to mitigate these effects. This goal will be achieved through the implementation of a comprehensive ambient particulate matter monitoring program in the Metropolitan St. Louis (IL-MO) area. The monitoring program is specifically designed to support state-of-the-art health studies and to provide atmospheric scientists and regulatory officials with the tools to efficiently and effectively develop particulate matter control strategies.

St. Louis is proposed as the Midwest Supersite for its favorable geographic situation, and for the opportunities it offers for integration with past and present air pollution studies. Metropolitan St. Louis is a major population center (2.5 million) well isolated from other urban centers of even moderate size, and is impacted by both distant and local sources. Local industry includes manufacturing, refining, and chemical plants. St. Louis is climatologically representative of the country's eastern interior, affected by a wide range of synoptic weather patterns and free of localized influences from the Great Lakes, Ocean, Gulf, and mountains. It accordingly provides an ideal environment for studying the sources, transport, and properties of ambient particles. Furthermore, these advantages have long been evident to field-study planners, resulting in a unique legacy of historical data.

During the 1970s, St. Louis hosted major studies of regional air quality (Regional Air Pollution Study, Trijonis and Eldon, 1980) and health effects (Harvard Six Cities study, Ferris et al., 1979). These data and cohorts will be available to the St. Louis Supersite program, leveraging the new measurements with historical context. They will provide a firm basis for qualitative comparisons between changes in particle concentrations and the emission reductions which took place during the last twenty-five years. More importantly, the existence of the cohort from the Six Cities Study in St. Louis will make it possible to assess the effect of cumulative ambient-particle exposures on the incidence of disease and life expectancy by prospective follow-up of a well-defined population.

The overall strategy of the proposed monitoring program was developed to address three overlapping particle research needs:

1. *Implementation and evaluation of highly time-resolved particle measurement techniques.* State-of-the-art continuous methods can now be used to measure aerosol number, size, and surface area (developed by the University of Minnesota), mass, sulfate and nitrate (developed by Harvard University), and elemental and organic carbon (developed by Sunset Laboratory). The use of these real or near-real time monitoring methods will make it possible to meet the St. Louis Supersite's quantitative data collection objectives in a cost-effective manner. The experience to be gained through the field testing of these monitoring techniques will be shared with the scientific and instrument manufacturing communities. This will be critical in the further development and evolution of these monitors, and will hopefully result in their application to large networks such as the EPA speciation network and other large air quality programs.

2. *Spatial and temporal (from minutes up to 24 hours) characterization of a large spectrum of particle physical and chemical properties in the St. Louis metropolitan area*. Besides the above-mentioned continuous monitors, a number of integrated samplers also will be employed to collect particles for fine and coarse mass, elemental analysis (including water soluble and non-soluble metals), organics, ionic species (sulfate, nitrate, ammonium, soluble sodium, soluble potassium, and particle acidity), and their gaseous precursors (nitric and nitrous acid, ammonia, and sulfur dioxide). These data will be merged with other air quality data sets such as particle mass (compliance network), particle composition (speciation network), gaseous co-pollutants (photochemical sites), and meteorological parameters. Collectively, these large data sets will be used as part of future investigations to develop source/receptor models, which ultimately will be used for setting up State Implementation Plans (SIPs). Also, this information will be critical in enhancing our understanding of sources, formation processes, and physico-chemical properties of ambient particles.

3. *Investigation of particle health effects.* The St. Louis Supersite program will be fully integrated with three large health effects programs: the EPA/Harvard Center on "Ambient Particle Health Effects: Exposure, Susceptibility and Biological Mechanisms", the NIEHS/Harvard Program Project on "Ambient Particles Cardiac Vulnerability on Humans," and the EPRI particle exposure assessment program. These three programs will support six research projects that will be conducted in St. Louis during the Supersite program. The six exposure and health effects studies (described below) constitute an ambitious research portfolio, which will greatly benefit from the Supersite program. The main objectives of these studies are the following: (i) investigate relationships between personal exposures and outdoor concentrations, and examine the health effects of chronic exposures; (ii) identify biological mechanisms responsible for particle health effects; (iii) identify susceptible populations; and (iv) investigate the relative toxicity of the different particle constituents.

To meet the objectives of the St. Louis Supersite program, a cost-effective monitoring strategy was developed. Our approach employs a stationary central site (the core site) in conjunction with a movable platform that will be used to conduct measurements at three satellite sites. At the core site, measurements will be conducted for a full year. For each satellite site it is anticipated that 21-24 consecutive days of sampling will be conducted during each of the four seasons. Because of the need to collect year-long data, the selection of the state-of-the-art sampling methods was based on their ability to operate for extended periods with relatively little attendance. For the same reason, it was decided not to include intensive studies in our program because they are costly and do not support several important health effect questions that need to be addressed.

The year-long daily data series will be analyzed for associations of excess mortality or morbidity with exposures to particles (mass, number, size, composition), and for seasonal and transport-related patterns in these exposures. The high time resolution proposed for the measurements will be of great value to both the source apportionment and health effects studies. Diurnal patterns such as the rush-hour peaks observed for certain species carry some source information relatively directly. Additionally, short-lived variations in the ambient mix improve the resolution of source apportionment methods that are limited by statistical collinearities in daily measurements. The satellite data will provide further resolution, in space, that will make it possible to investigate the impact of local sources and to assess community exposures to ambient particles. Finally, the use of continuous particle measurements in conjunction with the real time cardiac and other

biological measurements could make it possible to examine whether the time interval of the current short-term PM NAAQS – 24 hours – is appropriate.

A consortium of six universities was assembled to undertake the proposed St. Louis Supersite program. This group includes researchers from the Washington University (Principal Investigator Dr. Jay Turner and Dr. Warren White), Desert Research Institute (Drs. Judith Chow and John Watson), Harvard University (Dr. Petros Koutrakis), University of Minnesota (Dr. Peter McMurry), University of Maryland (Dr. John Ondov), and University of Wisconsin (Dr. James Schauer). In addition, Dr. Tina Bahadori from EPRI will be a collaborator in study. This research group has a great experience in the fields of methods development, particle chemistry and physics, field studies, data processing and analysis, source apportionment, exposure assessment, and quality assurance.

D.1.1. Background

The PM Supersites Program

The Environmental Protection Agency's "Supersites" program is an innovative response to the widely recognized need for a comprehensive characterization of airborne particulate matter in major U.S. urban centers. Supersites are intended to provide a more detailed physicochemical characterization of particles as compared to the particle mass compliance and speciation networks. This requires the development, field evaluation, and implementation of novel particle measurement techniques. In the process, a successful Supersite will support and enhance other important activities such as health effects and exposure research, atmospheric process modeling and source apportionment, and State Implementation Plan (SIP) development.

A Supersite is best conceived as a comprehensive regional monitoring program that is integrated into the national PM monitoring network. Because it serves multiple functions that go well beyond the needs of compliance monitoring, however, a Supersite is expected to leverage other governmental and private investments, and to have analysis and evaluation built into its design. Accordingly, while different Supersites should provide a core of consistent measurements, they are not required to be identical in their designs. It is essential that Supersites be designed as "learning" rather than "measurement" programs, with an emphasis on the diffusion of new information across traditional disciplinary boundaries.

The St. Louis Supersite Consortium

Washington University will be the lead institution for the St. Louis Supersite Consortium which includes nationally and internationally recognized experts in the field of particle physico-chemical characterization. This group was assembled to provide comprehensive, complementary research expertise and experience.

- Washington University (WU), led by Drs. Jay Turner (PI), Warren White, Edward Macias and Bret Schichtel, will be responsible for overall management of the Supersite program. Also, it will oversee the field operations, data analysis/interpretation, and the infrastructure for a state-of-the-art information support system.
- Desert Research Institute (DRI) of the University and Community College System of Nevada, led by Drs. Judith Chow and John Watson, will be responsible for ion analysis, quality assurance measures and data analysis.

- Electric Power Research Institute (EPRI), led by Dr. Tina Bahadori, will provide experience in project management and support (such as the ARIES program in Atlanta), private sector participation, and experience in exposure and health effects studies.
- Harvard University (HU), led by Dr. Petros Koutrakis, will be responsible for field sampling and analysis in support of the allied exposure and health effects.
- University of Maryland (UMCP), led by Dr. John Ondov, will be responsible for trace element sampling and analysis, including applications to source apportionment.
- University of Minnesota (UMN), led by Dr. Peter McMurry, will be responsible for aerosol physical characterization measurements.
- University of Wisconsin (UWI), led by Dr. James Schauer, will be responsible for carbonaceous species characterization such as organic compound speciation and EC/OC analysis, including applications of organic molecular markers to source attribution.

Earlier Studies

St. Louis was the focal point in the 1970's for several major field studies of urban and regional-scale air pollution. Two of these early studies included routine collection of fine particles on Teflon filters with the then-newly-developed dichotomous sampler. These studies provide a large data base on particle spatial and temporal patterns in the metropolitan St. Louis area, including mass concentration and chemical composition data obtained by methods similar to those used today. This unique legacy provides the proposed Supersite particle mass and composition measurements with historical context from a quarter-century earlier, including directly comparable baseline values.

The 1975-1976 Regional Air Pollution Study (RAPS) (Trijonis and Eldon, 1980) was a comprehensive U.S. EPA program to characterize transport and air quality in the metropolitan St. Louis area. A core element of this study was a network of 25 air monitoring stations distributed throughout the area. Ten of these stations included high-volume samplers collecting total suspended particles, and dichotomous samplers collecting inhalable (~PM_{20}) and fine (~$PM_{2.4}$) particles. The dichotomous samplers operated continuously for about 15 months. To resolve daytime and nighttime differences, eight of the dichotomous samplers collected 12-hour samples (2/day) and the remaining two samplers collected 6-hour samples (4/day). Even higher temporal resolution was obtained during an intensive campaign in summer 1976. All dichotomous sampler collection substrates were beta-gauged for mass and analyzed by X-ray fluorescence (XRF) for sulfur, major crustal elements, and selected trace metals. Network annual averages for 1976 are presented in Table 1 (all tables and figures are provided in Attachment D-I).

As part of the Harvard Six Cities Study (Dockery et al., 1993), personal exposure and respiratory health measurements of a 1300 person cohort in the Carondolet neighborhood of St. Louis started in 1975. Ambient monitoring for this study was collocated with the RAPS station in Carondolet. This site was not one of the ten stations equipped with dichotomous samplers during RAPS, so one of the RAPS dichotomous samplers was subsequently moved there. 24-hour integrated samples were collected from September 1979 to January 1987, at frequencies ranging from every day to every third day. Depending on the year, particle mass was determined using gravimetric analysis or beta attenuation; in addition, filter samples were analyzed using XRF or ion chromatography. The time series of annual averages from the Carondolet dichotomous sampler is presented in Table 2.

Along with the above studies incorporating routine dichotomous sampler measurements, several intensive field campaigns focused on atmospheric transport and transformation processes. In support of RAPS, the 1974-1976 Midwest Interstate Sulfur Transport and Transformation (MISTT) studies used instrumented aircraft and pilot balloons to map identifiable plumes of primary emissions and their secondary reaction products at ranges 100-150 km downwind of St. Louis (White et al., 1983). Concurrently, the collaborative 1971-1976 Metropolitan Meteorological Experiment (METROMEX) used sampling networks, instrumented aircraft, and radar to study the impacts of urban St. Louis on mesoscale airflow and precipitation (Changnon, 1978). While St. Louis emission rates have changed significantly since these field studies were conducted, the information they provide on the mesoscale behavior of these emissions remains largely valid, and will be helpful in the interpretation of data from individual monitoring stations.

Regulatory Compliance Monitoring

The historical as well as the ongoing (current) compliance monitoring network provides both context and support for the proposed St. Louis Supersite project. The St. Louis Metropolitan Statistical Area (MSA), Figure 1, includes air pollution monitoring programs operated by four agencies - City of St. Louis, St. Louis County, Missouri Department of Natural Resources, and Illinois Environmental Protection Agency. A large portion of the MSA is classified as moderate nonattainment for ozone. The city of Herculaneum (Jefferson County, MO) is classified as nonattainment for lead with sustained exceedances through 1996 and design values within 94% of the standard in 1997 and 1998. A small geographic area in Granite City (Madison County, IL) was formerly designated as moderate nonattainment for PM_{10} with a redesignation in 1998 as a maintenance area.

As part of its PM_{10} monitoring program, St. Louis County operated dichotomous samplers at several sites over the period 1988-1997. Data completeness for fine particulate matter reported to AIRS is highest for the Clayton monitoring site, which is a suburban area with its own central business district and is located about 15 km west of downtown St. Louis City. Annual average $PM_{2.5}$ mass concentrations for the Clayton site (Table 3) have remained steady at approximately 15 $\mu g/m^3$ for the last ten years and are very close to the current $PM_{2.5}$ annual standard.

$PM_{2.5}$ measurements commenced in January 1999 for the current U.S. EPA mass compliance monitoring network. By January 2000 there will be fifteen $PM_{2.5}$ mass monitor sites operating in the St. Louis MSA (Figure 2). Background monitors to the southeast (Houston, Randolph County, IL) and southwest (Bonne Terre, St. Francois County, MO) are about 60 and 85 km from St. Louis City, respectively. While three years of data has not yet been collected to determine compliance with the $PM_{2.5}$ standard, historical data as well as 1st and 2nd Quarter $PM_{2.5}$ monitoring suggests the urban core area is likely to violate the annual standard, with a relatively large geographic region being too close to call. Current plans call for sampling at up to four sites in the St. Louis MSA for the $PM_{2.5}$ Chemical Speciation Network. In addition, St. Louis has been selected as a sampler intercomparison site for $PM_{2.5}$ speciation monitoring; this sampling will commence in December 1999 at the City of St. Louis' Blair Street monitoring site.

Recent/Ongoing Particle Studies

Metropolitan St. Louis Fine PM Saturation Monitoring Study. Washington University (Dr. Jay Turner, Principal Investigator) recently conducted a $PM_{2.5}$ saturation monitoring study in the City of St. Louis and the near suburbs of St. Louis County. This project, funded by the Missouri Department of Natural Resources, was designed to elucidate neighborhood scale and urban scale

spatial-temporal patterns of $PM_{2.5}$ mass concentration. The objectives of this project were: to evaluate the local $PM_{2.5}$ regulatory network monitor siting plan; to provide insights into monitor zones of representation; and to support the development of a conceptual model for $PM_{2.5}$ behavior in the metropolitan St. Louis area. The saturation monitoring network included nine sites equipped with portable $PM_{2.5}$ samplers – five sites were fixed during the six-month study period and four sites were relocated every 4-6 weeks. Sampling was synchronized with the 1-in-3 day compliance network schedule. The saturation monitoring network also included collocated samplers, field blank samplers, and two collocated $PM_{2.5}$ FRM samplers (one of which operated daily). Sampling was conducted during the period March-October 1999. While the data analysis is still underway, preliminary results indicate that there is an urban-scale gradient in $PM_{2.5}$ mass radiating outward from a maximum concentration in the urban core region. Also, $PM_{2.5}$ mass tends to correlate with air mass history. For example, relatively low daily $PM_{2.5}$ levels (below 10 $\mu g/m^3$) are observed for fast-moving air masses arriving from the north/northwest, while relatively high daily $PM_{2.5}$ levels (in some cases approaching 50 $\mu g/m^3$) are observed for slow-moving air masses passing through the Ohio River Valley en route to St. Louis. Four such trajectories are shown in Figure 3.

Midwest Aerosol Characterization Study (MARCH-MW). This EPRI-funded study (Dr. Tina Bahadori, Project Manager) brings together several of the investigators for the proposed St. Louis PM Supersite to investigate the concentration and composition of fine particulate matter in the Midwestern United States. Lead investigators for this study include Dr. Petros Koutrakis (Harvard University), Dr. Judith Chow (Desert Research Institute), and Drs. Warren White and Jay Turner (Washington University). MARCH-MW was originally designed to examine the concentration and composition of $PM_{2.5}$ in six Midwestern urban environments. This study was intended to lay the groundwork for future SIP development and potentially a supersite-type monitoring program in the Midwest (similar to ARIES in Atlanta).

MARCH-MW featured a forty-day field study during the period August-September 1999, with daily sampling for $PM_{2.5}$ and PM_{10} mass, $PM_{2.5}$ chemical speciation and associated gaseous precursors (e.g., ammonia, sulfur dioxide and nitric acid). Sampling was simultaneously conducted in six Midwest cities: Athens (OH), Charleston (WV), Cincinnati (OH), Chicago (IL), Detroit (MI), and St. Louis. In a subset of these cities monitoring will be repeated in Winter 2000. The St. Louis monitoring site for MARCH-MW was the Margaretta Street site proposed for the St. Louis PM Supersite. Preliminary data from this campaign, available by Winter/Spring 2000, will help to refine our Supersite plans.

D.1.2. Exposure and Health Effects Studies Planned for St. Louis

A series of exposure assessment, epidemiological, and toxicological studies will be integrated into the St. Louis Supersite program. These investigations will be conducted as part of three currently funded research programs: the EPA/Harvard Center on ambient particle health effects (1999-2004, $7,500,000), the NIEHS/Harvard Program Project on ambient particles cardiac vulnerability in humans (1999-2004, $8,000,000), and the EPRI Exposure Assessment Research Program (2000-2002, approximately $1,000,000). Letters of commitment from the Center and Program Project principal investigators, Drs. Petros Koutrakis and Frank Speizer, as well as from the EPRI project manager, Dr. Tina Bahadori, are presented in Attachment D-II.

The six integrated research projects are described below. Each exposure assessment, epidemiological, and toxicological study will rely on the Supersite measurements and therefore will be coordinated with the Supersite program.

1. Measurements of Personal and Indoor Exposures to Particulate and Gaseous Air Pollutants. Principal Investigators: Drs. Helen Suh and Petros Koutrakis (EPRI exposure studies). The majority of air pollution epidemiology studies have relied upon exposure data obtained from outdoor stationary monitors. A large number of personal exposure studies are underway. The objective of these exposure studies will be to characterize the particulate and gaseous exposures of susceptible individuals. In addition, these studies will examine the relationships between personal exposures and outdoor concentrations and investigate factors affecting them; however, most of these investigations will be conducted in non-Midwestern U.S. urban environments such as Boston, New York, Baltimore, Atlanta, Los Angeles, and Seattle. If our proposal is accepted, EPRI will fund an exposure assessment study in St Louis which will make it possible to relate personal and indoor measurement data directly to those obtained from the Supersite. Two exposure studies will be conducted during the Supersite program: in the winter of (2000/01); and in the summer of (2001). A recently-developed multi-pollutant sampler will be used to measure fine particle mass, elemental and organic carbon, trace elements, sulfate, and nitrate, as well as ozone, sulfur dioxide, and nitrogen dioxide.

2. Cardiac Vulnerability in Potentially Susceptible Patients and Subjects. Principal Investigator: Dr. Frank Speizer (NIEHS Program Project). Much of the air pollution-related mortality and morbidity is associated with cardiovascular disease events. Therefore, concern has been raised as to the potential mechanisms whereby such effects can be explained. The effects to date have been associated with total particle mass. As part of this project, patients with well-characterized coronary heart disease will be identified and monitored. These selected groups will be monitored repeatedly for 48 hours with ambulatory EKG monitors to determine changes in heart rate, heart rate variability, and ST segment morphology. Using the personal, microenvironmental (from Project #1), and the Supersite ambient air quality measurements, the effect of particle physico-chemical characteristics on the cardiac parameters will be assessed. This study will be conducted during the winter of (2000/01) and summer of (2001) in conjunction with the personal exposure assessment studies. For each season, monitoring will last eight weeks. The retrospective analysis of samples for detailed organic speciation and trace metal composition (described in section D.2.) will include these periods.

3. Air Pollution and Implantable Cardioverter Defribrillators Detected Arrhythmias. Principal Investigator: Dr. Douglas Dockery (NIEHS Program Project). Patients with pre-existing cardiovascular disease are particularly at risk for acute response to particulate air pollution episodes. Implantable cardioverter defribrillator (ICD) devices monitor and identify heart arrhythmias and initiate therapeutic interventions when arrhythmias exceed predefined thresholds. The date and time of these events are stored, along with electrocardiographic recordings of the events triggering therapeutic interventions. These data will be abstracted for the St. Louis area to produce the number and types of arrhythmias that occur by date. Counts of arrhythmic events will then be compared to particulate data for the Supersite monitors. This study will provide quantitative exposure-response functions relating specific particle characteristics to the risk of cardiac arrhythmias, a precursor of acute cardiovascular failure

and sudden death. This project will be conducted in collaboration with the Washington University Medical School and will rely upon on the entire yearlong ambient air quality data set collected by the Supersite program.

4. Examinations of Conditions in the Elderly Which Predispose Towards an Acute Adverse Effect of Particulate Exposure. Principal Investigator: Dr. Joel Schwartz (EPA PM Center). Time series studies of the association of particle exposures with daily mortality have consistently shown stronger associations in susceptible individuals as compared to healthier populations. This project will test the hypothesis that patients with pre-existing respiratory, cardiovascular, or diabetic conditions have an enhanced mortality response to particles. In this project, elderly subjects from the St. Louis metropolitan area with a history of hospital admissions for respiratory and cardiovascular disease and diabetes will be identified using the Medicare database. This cohort will be tracked for deaths during an eighteen month period by searching the National Death Index. This study will use daily data from the Supersite.

5. Investigation of Chronic Effects of Exposure to Particulate Matter. Principal Investigator: Dr. Douglas Dockery (EPA PM Center). This project will assess the effects of air pollution exposure by extending follow up of adults in St. Louis, which is one of the Harvard Six Cities studies (the other five are Boston, MA, Steubenville, OH, Portage, WI, Kingston/Harriman, TN, and Topeka, KS). The prospective follow up of well-defined populations directly address the fundamental question regarding the effect of cumulative exposure to particulate air pollution on incidence of disease (cardiovascular disease, lung cancer, etc.) and life expectancy. St. Louis offers a unique cohort (of approximately 1,500 adults, 25-74 yrs) which has been tracked since 1974. Baseline respiratory health status, including pulmonary function, was assessed for each subject, as well as individual determinants of respiratory health status, including smoking history, occupational exposure, residential history, and treatment for chronic cardiovascular diseases. As part of the Harvard PM Center, the results of the St. Louis study will be analyzed along with the other five cities in order to investigate the chronic effects of exposures to particles.

6. *In Vitro* Toxicity of the St. Louis Particulate Matter. Principal Investigators: Drs. Les Kobzik and Petros Koutrakis (EPA PM Center). Recently the Harvard School of Public Health developed a High Volume Low-cut Impactor (HVLI). This impactor can be used to collect large quantities of coarse, fine, and ultrafine particles for toxicological studies. During the Supersite program, weekly samples will be collected using the HVLI. Subsequently, the collected particles will be used for *in vitro* bioassays. The bioassay tests to be undertaken will use rat alveolar macrophage cells which produce inflammatory mediators in response to particle toxic components. Relationships between particle composition (provided by the Supersite program) and particle toxicity will be investigated in an effort to identify particle components which can induce biological effects. Finally, a fraction of collected particles will be frozen and stored for future toxicological or chemical characterization studies.

In summary, a very ambitious particle health effects research portfolio will be developed around the St. Louis Supersite. The six research projects are well integrated and will be conducted by a large interdisciplinary group which has been working together for many years. We expect that the results of these six projects, in conjunction with those of the Supersite program, will enable us to relate mortality and mortality outcomes to specific particle physico-chemical properties.

Dr. Koutrakis, Co-PI, will act as a liaison between the Supersite program and the exposure and health effects researchers.

D.1.3. Leveraging of Resources

The St. Louis Supersite features extensive leveraging of resources:

- Six St. Louis-based exposure and health effects studies will be conducted in coordination with our particulate matter measurements (section D.1.2.). Approximately $2,000,000 of the $15,500,000 combined funding level for the EPA/Harvard Center and NIEHS/ Harvard Program Project will be spent on studies coordinated with the Supersite program.
- The EPRI-funded MARCH-MW field study – funded at over $1,000,000 – will collect baseline data for particle mass, composition and precursor gases for a forty day period in St. Louis.
- Sampling equipment will be used from the EPRI-funded MARCH-MW study, including particle mass and speciation samplers (described in section D.2.). ($50,000)
- Denuder/filter pack systems will be provided at no cost by Harvard University ($100,000).
- Instrumentation for measuring aerosol physical properties (described in section D.2.) will be transferred from the EPRI-funded ARIES study in Atlanta and also provided at no cost to EPA by the Particle Technology Laboratory at the University of Minnesota. ($175,000+)
- Sampling and analysis costs for particle mass and trace element composition (both water soluble species and bulk composition) will be funded from the NIEHS/Harvard Program Project in support of exposure and health effects project #2 and #3 described in section.D.1.2. ($100,000)
- Gaseous criteria pollutant data and $PM_{2.5}$ Chemical Speciation Network data collected by state/local agencies. In most if not all cases, our sampling platforms will be located at compliance monitoring network sites.

D.2. APPROACH

Measurements will be carried out at a fixed site in the City of St. Louis and from a movable platform (e.g., a trailer) that will be operated at three satellite sites. The measurements made at the fixed site (the core site) will be more detailed than those made at the satellite sites. This dual measurement strategy will enable us to sustain a detailed characterization of aerosol physical/chemical properties while simultaneously providing information for investigating spatial variability and the effects of transport. Simultaneous measurements at two points (the core site and a satellite site) will also permit investigations of time-series correlations between selected measurements at different sites.

Measurements at the core site will be phased-in starting in October 2000. All equipment – including the satellite site platform – will be operating by January 1, 2001. A full year of measurements will be conducted during the period January 1, 2001 through December 31, 2001. Our monitoring strategy is to provide year long measurements of a large number of physical and chemical particle parameters at the same site to support the health effects and source apportionment studies. Therefore, due to limited resources, we do not plan to include measurements that can only be operated during short intensive measurement periods, since we

feel that such measurements will contribute less to our understanding of aerosol health effects than those obtained over a more extended period of time.

The proposed measurements fall into two broad categories: those that can be obtained with minimal operator support on a continuous or semi-continuous basis (*in situ* measurements), and integrated filter or impactor samples that require laboratory analysis (substrate methods). Some of the laboratory analyses will be performed on all samples collected; other analyses will be performed on selected subsets of the integrated samples based on a retrospective analysis of meteorology and *in situ* particle data.

D.2.1. Sampling Sites

The proposed core site will be collocated with the City of St. Louis' Margaretta Avenue compliance monitoring station at Taylor Avenue and Margaretta Avenue. The site is located in a high-density, low-to-middle income urban residential area approximately 6 km northwest of the City of St. Louis' central business district (CBD) (Figure 4), and is designated as a Category "B" community-oriented (CORE) SLAMS site. Current measurements include daily $PM_{2.5}$ monitoring by City of St. Louis' Division of Air Pollution Control. Additionally, the State of Missouri recently received permission from U.S. EPA to move a suite of criteria pollutant monitors to this site from the Newstead Avenue site about 2 km to the south. Monitors to be moved during calendar year 1999 to the Margaretta site include ozone, sulfur dioxide, nitrogen dioxide, carbon monoxide, and PM_{10}.

Our core site measurement platform will be located next to the compliance monitoring site in an adjacent vacant lot also owned by the City of St. Louis. We will make improvements to the lot, including a security fence, electricity and telephone lines, and a utility shed to house the instruments. A letter of support from Dr. Timothy Dee, Commissioner for the Division of Air Pollution Control of the City of St. Louis, is presented in Attachment D-II.

The movable platform will be operated at three satellite sites. Seasonal measurements will be conducted at each site during the yearlong sampling program. Satellite sampling locations will be finalized in Spring 2000. In light of the objectives presented in section D.1., we anticipate establishing satellite sites: (1) upwind of the metropolitan area to characterize material transported into the City (candidates include Bonne Terre, MO, and Houston, IL); (2) in a suburban residential area to contrast with the Margaretta site urban residential area; (3) at a community-oriented site with predicted maximum $PM_{2.5}$ exposures (such as the City of St. Louis' Category "A" Blair Street site); and/or (4) at an area with significant localized anthropogenic emissions (such as an industrialized area or the City of St. Louis' CBD). Several criteria will be used to rank the proposed satellite sites, including but not limited to: number and relative importance of study objectives which can be addressed; proximity to compliance network monitors and/or particle speciation network monitors; proximity to sites used in earlier studies (e.g., RAPS, Six Cities Study); and accessibility and security. U.S. EPA has proposed to fund an additional 5-to-6 particle speciation network sites in each Supersite domain. Depending on the locations selected for these sites, it may be possible to collocate each satellite site with a chemical speciation network site.

We anticipate at least 21-24 consecutive days of sampling during each of the four visits to a satellite site. The balance of time will be needed to relocate the trailer and set up for measurements. Letters of support from Missouri state and local air pollution control agencies

(St. Louis City, St. Louis County, Missouri Department of Natural Resources) are presented in Attachment D-II. We also expect to partner with the Illinois Environmental Protection Agency during this project.

D.2.2. Ambient Measurements and Analyses

In this section we discuss our proposed measurement plan. Physical and chemical properties will be measured using both *in situ* and substrate methods. Key meteorological variables will also be measured. In developing this plan we focused on measurements that could be used to test hypotheses regarding factors that may influence human health and to infer impacts of various sources on local aerosol physical and chemical properties. This measurement plan also satisfies the minimum data collection objectives presented in the Supersite program solicitation.

We make a particular effort to include physical and chemical aerosol properties that can be measured *in situ* (continuously or semi-continuously) because such data may provide important new clues about health effects and emissions sources. In some cases we will utilize instruments with an established record for reliable, unattended operation for extended periods of time. In other cases, we plan to use instruments that have shown promise but have not yet been proven for long-term continuous measurements (e.g., the aerosol integral moments packages). We anticipate that this approach will enable us to advance the state-of-the-art for routine monitoring of ambient air quality while simultaneously providing valuable new insights into aerosol properties.

Many aerosol constituents that may play a role in health effects cannot be measured continuously. For such constituents we plan to collect time-integrated samples for later characterization in the laboratory. Because certain off-line analyses are expensive, we have established a pragmatic sampling and analysis strategy that will be sustained throughout the yearlong measurement period. All samples will be stored for possible analysis in the future. All time-integrated samples corresponding to the $PM_{2.5}$ speciation network measurements will be analyzed with daily frequency. For the remaining methods, a retrospective analysis of the meteorological data, *in situ* aerosol data, speciation network type data, and available health effects data will be used to select samples for analysis.

In the remainder of this section we summarize the following types of measurements:

- aerosol physical characterization measurements;
- aerosol mass measurements (*in situ* measurements and substrate methods);
- sustained aerosol chemical characterization (*in situ* measurements and substrate methods);
- detailed trace metals speciation for a subset of samples;
- detailed organic compound speciation and thermal analysis for a subset of samples; and
- other measurements, including toxicological sampling, gaseous pollutants, meteorology.

The proposed measurements are presented in Table 4.

Aerosol Physical Characterization

Details of the ambient aerosol size distribution can be used to investigate emissions and atmospheric processes. Health effects studies are more likely to use integral moments of the

size distribution as indicators (such as the aerosol number, surface area, and mass concentration). There probably exist conditions for which these indicators are highly correlated and conditions for which their correlation is low. A key objective of our program is to measure both detailed aerosol size distributions and integral moments with high temporal resolution. In addition to directly supporting atmospheric science and health studies, this data will be used to investigate the ability to reconstruct aerosol size distributions from integral moment measurements. It will also be used to determine the conditions (such as meteorology) which significantly influence the degree of correlation between typical indicators for aerosol physical properties.

The University of Minnesota team will be responsible for designing the instrument package for continuous measurements of aerosol physical properties and for processing data from these instruments. A summary of the proposed measurements is provided in Table 4a. To reduce costs and minimize manpower requirements, size distributions will be measured only at the core site. The system used here will be similar to that used for continuous measurements from August 1998 through December 1999 in Atlanta as part of the EPRI-funded ARIES program. Measurements from four instruments will be merged into a single size distribution covering the 3 nm (0.003 µm) to 10 µm diameter range using software developed at the University of Minnesota. Contour plots illustrating continuously measured size distributions in Atlanta are shown in Figure 5.

Two scanning mobility particle sizers (Knutson, 1976; Fissan et al., 1983; Keady et al., 1983) will be used to measure size distributions in the 3 nm to 500 nm diameter range. These instruments classify particles according to electrical mobility equivalent diameter that depends on geometric size and shape. For spherical particles, the electrical mobility equivalent diameter equals the geometric size. These instruments have reliably provided continuous measurements of size distributions for nearly a year in the ARIES project. The Scanning Mobility Nano-Particle Spectrometer (nano-SMPS) utilizes a commercially available electrostatic classifier optimized for particles in the 3-20 nm diameter range. The prototype for this instrument was developed at the University of Minnesota (Chen et al., 1998). Concentrations of classified particles will be measured with the TSI 3025 ultrafine particle condensation counter (CPC) that is also based on a design developed at the University of Minnesota (Stolzenburg and McMurry, 1991). The nano-SMPS permits for the first time accurate measurements of size distributions of such particles. This is of interest, for example, since recent emissions testing research has shown that new technology diesel engines can emit high concentrations of particles in the 5-10 nm diameter range (Bagley et al., 1996). Both the SMPS and nano-SMPS units will be provided from the EPRI-funded ARIES study in Atlanta.

The optical particle counter (OPC) and aerodynamic particle sizer (APS) both provide information on particles in the 0.3 to 2 µm diameter range where most fine particle mass is found. This redundancy is intentional. OPCs measure a “light scattering equivalent” size that is dependent on a particle’s refractive index and shape. Although such instruments have often been used for atmospheric measurements, and while some information on shape and refractive index that can be used to interpret such measurements is available (Dick, 1998), uncertainties remain regarding measurement accuracy (McMurry, 1999). The aerodynamic particle size measured with the APS depends on particle size, shape and density. Only a limited amount of information on densities for atmospheric particles is available (Stein et al.,

1994). One objective of our Supersite program is to use parallel measurements of ambient aerosols over an extended period to evaluate the relative merits of these instruments. The OPC from the EPRI-funded ARIES project will be used in St. Louis.

In order to obtain variables that can be used to test health effects hypotheses, we propose to calculate time-averaged integrals over specified size ranges. For example, for ARIES we report hourly averaged values for number concentration, surface area concentration, and volume concentration in the 3 nm to 10 nm, 10 nm to 100 nm and 0.1 µm to 2 µm diameter ranges. This dramatically reduces the size of the data set and puts data in a convenient form for hypothesis testing.

During the past several years, Dr. David Pui and coworkers at the University of Minnesota were supported by U.S. EPA to evaluate the use of integral moment measurements to infer essential features of the submicrometer aerosol size distributions (Whitby, 1978). In theory, such measurements can provide much of the information that is obtained from detailed measurements of size distributions at a small fraction of the cost and effort. One of our Supersite goals is to investigate the utility of such measurements for routine monitoring. Based on work already completed at the University of Minnesota we plan to construct two prototype units, each of which will measure three integrals: total number concentration, total electrical charge downstream of a diffusion charger (Chen and Pui, 1999), and the dry light scattering coefficient (Anderson et al., 1996). The number concentration is dominated by particles smaller than 100 nm, the electrical charge is weighted by particles somewhat larger than this, and the dry light scattering coefficient varies nearly in proportion to dry aerosol mass concentration (Charlson et al., 1968) which typically peaks in the 300-700 nm range. By measuring these integrals in parallel with complete size distributions we will be able to determine the accuracy with which size distributions can be reconstructed from measured integrals (moments). Furthermore, we will obtain hourly averages of the integral moments for use in health effects studies, and will carry out time series correlations at the core and satellite sites to determine which moments are correlated and which are not. The ultrafine condensation particle counter sensors to be used to measure total number concentration will be provided by the University of Minnesota Particle Technology Laboratory, at no cost to U.S. EPA.

Figure 6 shows total aerosol surface area concentrations of ambient aerosols during a 20 day period in Minneapolis calculated from measured detailed size distributions and estimated from measurements of the three integral moments mentioned above. Note that the surface areas inferred from the moment method are in good agreement (±10%) with the actual values for all but 3 of the 20 days on which measurements were carried out. The size distribution data indicated that concentrations of soil dust were elevated on the days when the two methods agree to only 30%. A full year of continuous data will be collected at the St. Louis Supersite to comprehensively evaluate the potential of integral moment measurements to reconstruct key features of ambient aerosol size distributions.

In addition to the University of Minnesota-based measurements, Harvard University will be responsible for two *in situ* integral moment measurements at both the core and satellite sites. The aethalometer will be used to measure "optical density" by the transmittance of aerosol deposits collected on filters (Hansen et al., 1984). Because transmittance is primarily sensitive to absorption, and soot (black carbon) is the primary absorbing species in urban areas, these measurements provide a sensitive indicator of local soot concentrations. These

measurements provide high temporal resolution and can be evaluated by comparing time-averaged values to the hourly-average and daily-average elemental carbon measurements described below. The Continuous Ambient Mass Monitor (CAMM), described in the next section, will be used to obtain hourly-average aerosol mass.

Aerosol Mass Measurements

Given that mass concentration is the indicator for $PM_{2.5}$ compliance monitoring, we give significant attention to such measurements. Our plan includes both continuous and 24-hour integrated substrate methods, with the latter obtained using a $PM_{2.5}$ FRM and also relatively inexpensive impactors that achieve FRM-like performance. Harvard School of Public Health (HSPH) will be responsible for the instrumentation packages and data processing for aerosol mass measurements except as noted.

In-Situ Measurements. $PM_{2.5}$ mass will be continuously measured at both the core and satellite sites using the Continuous Ambient Mass Monitor (CAMM). This unit has recently been developed at HSPH (Babich et al., 1999; Sioutas et al., 1999) and is being commercialized by Andersen Instruments. The method is based on the measurement of the pressure drop increase across a membrane filter during particle sampling. The monitor consists of a conventional impactor/inlet to remove particles larger than 2.5 µm, a diffusion dryer to remove particle-bound water, a filter tape to collect particles, a filter tape transportation system to allow unassisted sampling, and a data acquisition and control unit. Features are built into the design to minimize volatilization and adsorption artifacts during sampling. Furthermore, since the flow rate for the fine particle mass monitoring channel is very low (0.3 L/min), the relative humidity of the air sample can be easily reduced to 40% or less using a Nafion™ diffusion dryer to remove particle-bound water. This is important because U.S. EPA protocols for substrate methods include sample equilibration at a controlled relative humidity. The CAMM has a detection limit of less than 3 $\mu g/m^3$ for $PM_{2.5}$ concentrations averaged over one hour. Time-averaged CAMM measurements were compared to Harvard Impactor (HI) 24-hour $PM_{2.5}$ integrated measurements for 211 sampling days in several cities and different seasons. The HI and CAMM $PM_{2.5}$ were highly correlated ($r^2 = 0.90$), with an average CAMM-to-HI concentration ratio of 1.07 ± 0.18 (Babich et al., 1998).

Substrate Methods (24-Hour Integrated Sampling). Harvard Impactor (HI) samplers will be used at both the core and satellite sites to obtain particle mass concentrations for PM_{10}, $PM_{2.5}$ and PM_1 size ranges (Marple et al., 1987; Lioy and Wainman, 1988; Turner et al., 1999). The HI is a relatively low flow particle sampler (10 L/min) that uses an oiled impactor plate to minimize particle bounce and provide a sharp cut point, giving measurements similar to U.S. EPA reference methods. Particle mass concentration is calculated from the mass change of a filter (located downstream of the impactor during sampling) by precision weighing under controlled conditions. HI samplers have already been procured through the EPRI-funded MARCH-MW study, and gravimetric analysis will be funded by the HSPH NIEHS Program Project. Another time-integrated $PM_{2.5}$ mass measurement at both the core and satellite sites will use the Teflon filter from HEADS sampler (described in the next section). Additionally, the City of St. Louis operates a $PM_{2.5}$ sequential FRM (daily frequency) and will be moving a PM_{10} sampler (1-in-6 day frequency) to the core site.

One goal of our Supersite program is to evaluate alternative methods for quantifying coarse mass (CM, defined as PM_{10} - $PM_{2.5}$). The HI collects particles on filters arranged in parallel rather than using a cascade impactor arrangement. This is important because CM determined by difference from HI-based measurements has recently been shown to be more precise than CM obtained from a dichotomous sampler (Allen et al. 1999). We will also operate a high-resolution dichotomous sampler at both sites to further investigate this finding.

Sustained Aerosol Chemical Characterization

Both semi-continuous measurements and time-integrated substrate methods will be used to determine aerosol chemical composition. The proposed measurements are presented in Table 4b. Several groups will be responsible for the measurements, including HSPH, Desert Research Institute (DRI), the University of Maryland (UMCP) and the University of Wisconsin (UWI). This section summarizes those measurements and analyses which will be sustained throughout the yearlong monitoring program. The subsequent two sections describe time-resolved trace metal speciation and organic compound speciation, respectively. Sustained hourly-average trace metal speciation will be performed for five elements with an additional twelve elements analyzed for a large subset of the collected samples. Organic compound speciation will performed on a large subset of 24-hour integrated samples collected everyday.

In Situ Measurements. Semi-continuous monitors for fine particle sulfate, nitrate, and elemental and organic carbon will be used to determine concentrations of these species throughout the entire year-long sampling program with a time resolution of one hour or less. Particulate nitrate and sulfate monitors will be used at both the core and satellite sites. These instruments are still under development, with many candidates being tested at the Atlanta and Fresno Supersites. A preliminary evaluation of candidate instruments for these measurements has been completed based on initial instrument performance results and the data requirements of the proposed project, and the instrument developed by the Harvard School of Public Health has been tentatively selected. However, this evaluation will be revisited prior to purchasing instruments for the St. Louis Supersite.

The continuous Elemental and Organic Carbon (EC/OC) instrument selected for this project is currently in the final stages of development by Sunset Laboratories. This instrument is a second-generation continuous EC/OC analyzer that is based on the design originally reported by Turpin et al. (1990). It utilizes the analyzer section of the lab-based EC/OC analyzer that is specified by both NIOSH Method 5040 and particle speciation network (U.S. EPA RFP # PR-NC-98-11738). The selection of the Sunset Laboratory analyzer is driven by the desire to make the continuous EC/OC measurements consistent with the particle speciation network methodology and the source emissions profiles that will be used for receptor modeling calculations. The continuous EC/OC analyzer will be operated to obtain hourly averaged measurements with a minimum detection limit of 0.5 $\mu g/m^3$ or lower. It will incorporate organics denuders to obtain artifact-free EC/OC measurements and will utilize two sample collection chambers for continuous operation. Attachment D-II includes a letter of commitment from Sunset Laboratories to deliver the continuous EC/OC analyzer for use in the St. Louis Supersite program. Due to the developmental nature of this instrument, it will be operated at the core site only.

Substrate Methods (24-Hour Integrated Sampling). Analysis of 24-hour integrated samples collected everyday at both the core and satellite sites will provide several enhancements with

respect to the U.S. EPA particle speciation network protocols, including: (1) analysis for precursor gases; (2) additional target species for the ion analysis; (3) elemental analysis using high resolution methods; and (4) determination of water soluble-metals concentrations. In some if not all cases, the satellite site will be located at particle speciation network sites to provide a direct comparison between our measurement strategies and the standard network methods. Samples will be collected in parallel with the continuous sulfate and nitrate analyzers at the core and satellite sites, and in parallel with the continuous EC/OC analyzer at the core site. Time-average concentrations from the continuous monitors will be compared to the 24-hour integrated data from the substrate methods. Substrate method measurements will be phased-in as early as October 2000 at the core site to provide 15 months of sustained data; seasonal measurements at the satellite sites will be conducted over a 12 month period.

Carbon. EC/OC samples will be collected downstream of an organics denuder on baked quartz-fiber filters (Tissuequartz, Pall-Gelman). The filters will be analyzed by the University of Wisconsin using a Sunset Laboratory laboratory EC/OC analyzer.

Ions and Precursor Gases. Under the direction of the HSPS team, the Harvard/EPA Annular Denuder System (HEADS) will be used at the core and satellite sites to collect 24-hour integrated samples to simultaneously measure several atmospheric pollutant gases (SO_2, HNO_3, HNO_2, and NH_3) and inorganic fine particulate ions (SO_4^{2-}, NO_3^-, H^+, Na^+, K^+ and NH_4^+) (Koutrakis et al., 1988; Brauer et al., 1989; Koutrakis et al., 1990; Koutrakis et al., 1992; USEPA-ORD, 1992). The equipment has already been purchased by EPRI for the 1999 MARCH-MW study. Sample analysis for the precursor gases and inorganic ions will be conducted by DRI.

The HEADS sampler draws air at 10 L/min through a glass impactor inlet which removes particles larger than 2.1 µm, and then through two annular diffusion denuders in series. The first denuder is coated with sodium carbonate which collects the acidic gaseous species nitrous acid (HNO_2), nitric acid (HNO_3) and sulfur dioxide (SO_2). The second denuder is coated with citric acid which collects ammonia (NH_3). These denuders are designed to minimize particle losses to the walls. After passing through the denuders, the fine particles are collected on a Teflon filter in the front of a filter pack. Nylon and citric acid-coated glass fiber filters are placed in series downstream of the Teflon filter to collect HNO_3 and NH_3, respectively, that have volatilized from the collected fine particles. All species, both gaseous and particulate, are determined by either ion chromatography (IC) or by pH (H^+) measurement. The HEADS method has been extensively tested and compared to related sampling and analytical techniques (Ellestad et al., 1991). It has been used in several research studies over the last seven years and has been published as an EPA standard method (USEPA-ORD, 1992). Table 5 summarizes the performance of HEADS.

Trace Elements. Analysis for trace elements will be performed on $PM_{2.5}$ samples collected everyday at the core and satellite sites using Harvard Impactors (HI). To facilitate the analytical methods intercomparison which is described below, five 24-hour integrated $PM_{2.5}$ samples will be collected at the core site each day and two 24-hour integrated $PM_{2.5}$ samples will be collected at the satellite site each day. One of the samples collected daily at each site will be used to quantify the water-soluble trace metals using a water extraction procedure and Inductively Coupled Plasma Mass Spectrometry (ICPMS) analysis; this work will performed by a laboratory subcontracted by HSPS and funded through the NIEHS Program Project. The remaining samples will be designated for total trace elements quantification.

Historically, X-ray fluorescence (XRF) has been used as the prevailing analytical tool to measure trace metals in atmospheric particulate matter. Such analytical efforts have shown to be a powerful tool for the characterization of atmospheric TSP and PM_{10} samples. Due to the significantly lower loadings of these metals in atmospheric $PM_{2.5}$ samples as compared to TSP and PM_{10}, however, the usefulness of traditional XRF analysis for characterizing $PM_{2.5}$ samples is limited. XRF detection limits are not sufficient to measure many potentially important elements present in 24-hour integrated fine particle samples collected at 10 L/min. To this end, there is significant motivation to explore alternative analytical methods for quantifying trace metals in fine particle samples. In efforts to explore alternative methods, the benefits of XRF should not be forgotten. XRF analysis is fairly cheap, reasonably nondestructive, and can in principle get quick turnaround times. For this reason, efforts will be pursued to improve the detection limits of XRF by using high-resolution analysis protocols developed by DRI. In addition, Inductively Coupled Mass Spectrometry (ICPMS), Instrumental Neutron Activation Analysis (INAA) and Graphite Furnace Atomic Adsorption (GFAAZ) will also be pursued. Since these methods have various strengths and weaknesses, 40 samples collected with the collocated samplers at the core site will be retrospectively analyzed using: (a) high-resolution XRF analysis by DRI; (b) INAA by the University of Maryland; (c) GFAAZ by the University of Maryland; and (d) ICPMS by the University of Wisconsin using an aggressive extraction protocol. This inter-comparison effort will be used to rigorously assess the benefits and compromises associated with each analytical method. These results will be used to select a method that will be used to analyze one set of the remaining 24-hour integrated $PM_{2.5}$ samples collected at the core site and one entire set of $PM_{2.5}$ samples collected at the satellite site. A subcontract to conduct this elemental analysis will be provided by HSPS with funding from the NIEHS Program Project.

Elemental analysis for the coarse particle composition of daily samples will follow after we have completed the analytical methods intercomparison (described above) and resolved the preferred method for determining coarse particle mass (described in the aerosol mass measurements section under the substrate methods). A subcontract to conduct this elemental analysis will be provided by HSPS with funding from the NIEHS Program Project.

PM-2.5 Trace Metals Speciation

The previous section described elemental analysis for 24-hour integrated samples to be collected at the core and satellite sites. However, applications such as exposure and health effects studies and source apportionment studies would benefit from measurements taken with greater temporal resolution. For example, Lioy et al. (1989) have shown that the number of sources that could be resolved with principle component analysis increased when sampling times were reduced from 24 hours to shorter periods such as 12 hours and 6 hours. While it might be possible to reduce sample integration times using classical substrate-based sampling and analysis strategies, about six hours is generally assumed to be a lower limit to obtain quantifiable mass concentrations of trace metal species. These sampling times are much longer than the time scales for changes in source strengths and important meteorological parameters such as wind direction, mixing height, temperature, and relative humidity. The accompanying homogenization of source signals by this time-integration severely reduces the resolving power of correlation techniques (e.g., multilinear regression and factor analysis). It is likely that much higher temporal resolution, such as one hour or less, would permit resolution of individual, meandering plumes. Hourly resolution for

trace metal speciation would also support time-resolved exposure and health effects studies (e.g., study #3 in section D.1.2 of this proposal).

For these reasons, we propose to implement a novel sampling and analysis system to quantify selected trace elements at the core site in this study. Hourly-average $PM_{2.5}$ samples will be collected during the entire 12 month sampling period using the University of Maryland High-Frequency Aerosol Slurry Sampler (HFASS). This instrument was recently developed under a U.S. EPA STAR Grant awarded to the University of Maryland at College Park (UMCP) in collaboration with the Harvard School of Public Health (Kidwell et al., 1998). Samples collected using HFASS will be preserved for retrospective analysis to be conducted using a graphite furnace atomic absorption spectrometer at the University of Maryland. Samples will be selected for analysis according to the criteria defined in section D.2.3.; we propose to analyze at least 1200 samples (nominally 50 days of twenty-four 1-hour average samples) retrospectively for at least twelve elements as described below. These trace element analyses will be coupled with the 1-hour average carbon and sulfate measurements to provide a data set to support: unprecedented resolution of sources by receptor modeling techniques; detection of plumes from individual stationary sources; distinction of local from regional sources; and an estimation of local secondary sulfate formation rates. UMCP will be provide the HFASS system, analyze the samples, and process the data.

Elemental analysis will be conducted using atomic absorption spectrometry. Analyses are generally grouped in suites of 4-to-5 elements according to the commercially available multielement lamps. The relevant groups include As/Cu/Mn/Ni/Cr, Cd/Se/Ag/Pb, Al/Fe/Zn/Ca, and V/Ti/Be/Ba. One group has been identified to be of particular interest - As/Cu/Mn/Ni/Cr – based on the following application. In support of its St. Louis Community-Based Environmental Partnership (CBEP) program, U.S. EPA Region VII recently conducted a preliminary analysis using 1996 TRI data for on-site air releases to determine the top ten HAPs in St. Louis in terms of emissions and risk. This study ranked elemental manganese highest among all the HAPs from a risk-related perspective. Manganese compounds were tied for 4^{th}-highest, and chromium compounds and elemental chromium were ranked 7^{th} and 8^{th}, respectively. Indeed, all five elements in the suite we have selected are classified as Hazardous Air Pollutants (HAPs). Our proposed monitoring program will significantly enhance the efforts of U.S. EPA Region VII to implement a risk-based air screening analysis in St. Louis through the CBEP program by providing data for comparison to the modeling results. It will also support the broader objectives of the Unified Air Toxics program. For these same reasons, the data will be valuable to the health effects community. Indeed, the remaining elemental suites will be selected in consultation with health scientists to best serve their data needs. The options include criteria pollutants, metal-based hazardous air pollutants, and first series transition metals which are known or suspected to elicit respiratory inflammation.

The HFASS unit consists of a dynamic aerosol concentrator in which particles are grown by condensation of water vapor to facilitate separation from the air stream. Given the relatively low ambient concentrations of certain elements of interest (e.g., on the order of 0.1 ng/m^3 for Cd, Co, and Ag, and on the order of 1-5 ng/m^3 for As, Cr, Mn, Pb, Sb, Se, and V), $PM_{2.5}$ is sampled at a high flowrate (200 L/min) and delivered to an auto-sequencing sample collector for off-line analysis. While sampling times of less than ten minutes typically collect enough particulate matter in urban environments to permit a robust analysis (including triplicate measurements for each element), this unit will be operated for 1-hour integrated samples to achieve a balance

between high temporal resolution and costs which scale with the number of analyses. Detection limits for 1-hour integrated samples are summarized in Table 6. During laboratory analysis, reagent blanks and standards will be run several times each day. NIST Standard Reference Material 1648 ("Urban Particulate Material") has been used to test the method accuracy for nine of the elements to be quantified, with additional tests currently being conducted for the remaining elements of the list detailed above. Field testing of the instrument was conducted during summer 1999 in College Park, MD, and at the Atlanta Supersite in August, 1999.

PM-2.5 Organic Compound Speciation

Receptor modeling techniques have been recently developed that use specific organic compounds as molecular markers to apportion source contributions to atmospheric fine particle mass and atmospheric fine particle organic carbon concentrations (Schauer et al., 1996; Schauer and Cass, 1999; Schauer, 1998). Recognizing the power of this apportionment technique to elucidate the origin of atmospheric fine particulate matter, the U.S. EPA has incorporated the analytical procedure used by Schauer et al. (1996) in the U.S. EPA $PM_{2.5}$ Chemical Speciation Network (U.S. EPA RFP# PR-NC-98-11738). This analytical procedure has been used in the past to quantify both the organic tracers used for receptor modeling and other important organic compounds present in the fine particle source and ambient samples. A collaborative effort between the U.S. EPA and the University of Wisconsin-Madison (UW-Madison) is currently underway to further enhance this analytical procedure by preparation of new internal standards and quantification standards, as well as improved QA/QC through an inter-comparison effort between laboratories. The improved methodology and standards will be employed for the analytical efforts conducted by UW-Madison for the proposed St. Louis Supersite project.

The University of Wisconsin will be responsible for carbonaceous particulate matter sampling protocols, chemical characterization and data processing and analysis. Fine particulate matter samples for organic compound speciation will be collected with a high-volume cyclone based sampler which incorporates a high capacity organics denuder and a back-up adsorbent trap. The sampler is designed for the collection of fine particulate matter, which is suitable for the analysis of trace organic compounds in 24-hour samples. It is based on a commercially available sampler originally built by URG Inc. for the U.S. EPA. The sampler employs a URG Teflon coated cyclone that when operated at 91 lpm provides an aerodynamic aerosol 50 percent cut point of 2.5 µm. Likewise, the sampler uses a URG filter holder that will be loaded with baked quartz fiber filters. The URG version of the sampler employs a URG annular denuder located downstream of the cyclone and upstream of the filter, along with a PUF cartridge located downstream of the filter holder. The URG sampler uses a larger version of the XAD-coated denuders originally developed by Gundel et al. (1995) and used by Schauer et al. (1999a and 1999b) and Schauer (1998) with a dilution source sampler to make source emissions measurements. Although the smaller XAD-coated denuders have been shown to be well suited for the collection of semi-volatile organic compounds present in diluted source emissions, the larger version of the denuders is not appropriate for the sampling needs of the Supersite project proposed here. The XAD-coating process used for these denuders does not produce a denuder coating that has sufficient adsorption capacity to be continuously operated without reconditioning for the desired 24-hour sampling period, and replacing reconditioned denuders at more frequent periods is impractical. In addition, the large URG denuders are made of glass and are extremely expensive such that they are not compatible with large-scale field sampling projects. Finally, the denuder coating process is performed by a batch process that is very

difficult to implement in a manner that can assure consistent coatings between different coating batches. For these reasons, the XAD-coated URG denuders do not fit well with the needs of the proposed Supersite project and alternative sampler configurations are being pursued. Two alternatives employ different types of denuders that are better suited for the high-volume organics sampler and a third alternative eliminates the use of an organics denuder. The alternatives that are being reviewed are listed below:

- *Sunset Labs/Restek Denuder*: An organics denuder is being developed by Sunset Labs in collaboration with Restek Corp. The denuder uses a passivated metal annular denuder that is commercially coated with Haysep D resin using a proprietary cross-linking binding process. Haysep D resin is similar to XAD-4 resin. The denuder has advantages over the XAD-coated URG denuder in that the Sunset Labs/Restek denuder cannot be easily broken, the resin coating can be applied at any specified thickness using a highly reproducible commercial process, and the denuder can be procured at reasonable cost. The Sunset Labs/Restek denuder has demonstrated excellent performance in preliminary tests demonstrating high semi-volatile collection capacity, low particle losses, and an ability to be effectively reconditioned. These denuders are currently undergoing advanced testing at the University of Wisconsin-Madison by Prof. Schauer's Research Group. The Sunset Labs/Restek denuder system, if selected as the Supersite sampler, will include a PUF cartridge downstream of the Cyclone/Denuder/Filter system. The PUF cartridge will contain two PUF plugs (7.5 cm diameter by 7.5 cm long) operated in series. The PUF plugs are sized based on the compiled work by You and Bidleman (1984), Fraser et al. (1997), and Schauer et al. (1999a).
- *Activated-Carbon Denuder*: In the unexpected case that the Sunset Labs/Restek does not meet all of the performance requirements of the Supersite organics denuder, an activated charcoal-impregnated filter paper denuder (Eatough et al., 1993) will be pursued. Activated-carbon denuders have been shown to have high adsorption capacity for the collection of semi-volatile organic compounds, but do not allow the possibility of recovering the semi-volatile organic compounds collected by the denuder. The analysis of the semi-volatile organic compounds is desired since these compounds can be used as atmospheric tracers, they are likely precursors to secondary organic aerosols (SOA), and provide additional information on the partitioning of organic compounds between the gas and particle phases. If selected, the activated carbon denuder sampler will employ the same cyclone, filter assembly, and PUF cartridge as planned for the Sunset Labs/ Restek denuder sampler.
- *Filter/PUF Configuration*: The final potential organic aerosol sampler eliminates the use of an organics denuder and would be employed if the Sunset Labs/Restek denuder was unable to perform as needed and the activated-carbon denuder was deemed unacceptable due to loss of semi-volatile organic compound data. Although this configuration is susceptible to semi-volatile organic compound sorption artifacts on the quartz fiber filter, this sampling configuration is being considered for the EPA Fine Particle Chemical Speciation Network (Morton, 1999). The Filter/PUF sampler would use three PUF units due to the need for a higher collection capacity for semi-volatile organic compounds without the upstream denuder.

Samples will be collected every day at the core site, and 30 percent of the samples will be analyzed as part of the retrospective analysis. Table 7 presents a list of the target organic compounds that will be quantified. The list includes the molecular markers used for source apportionment, as well as organic compounds which are believed to be biologically significant and compounds which are typically found in high concentrations in ambient fine particulate

matter. A subset of the denuder extracts will also be analyzed as part of the retrospective analysis.

The proposed organic compound speciation measurements will provide the first detailed characterization of fine organic aerosols in the Midwestern United States, as most of the previous efforts to characterize the broad range of compounds shown in Table 7 have been limited to particulate matter collected in California with a few current efforts in the Northeastern United States and the Southeastern United States. In addition, the previous efforts to speciate the organic compounds in fine particulate matter have not been integrated into health effects studies as proposed for the St. Louis Supersite. This will allow epidemiologists to explore the health effects associated with organic compounds and sources of organic carbon. In addition to supporting health effects studies, the speciation of particle-phase organic compounds will also be used for source apportionment calculations. Since the organic compound speciation efforts will be performed under the direction of Dr. James Schauer, the ambient measurements will be consistent with several large source testing efforts that have been conducted in the past and that are currently underway at the California Institute of Technology, the University of Wisconsin-Madison, the University of California at Riverside, and the U. S. EPA. Such consistency is necessary for molecular marker source apportionment modeling. Source profiles for many important sources of fine organic aerosol in St. Louis have already been generated using the same analytical techniques as will be used in the proposed project (Schauer et al. 1999a; Schauer et al., 1999b; Schauer, 1998). In addition, significant effort is currently underway by the organizations listed above to generate additional source profiles that are important to St. Louis. These results will be available to the current project for use in molecular marker source apportionment efforts.

Although the source apportionment techniques provide a powerful tool to understand the origin of airborne fine particulate matter, the time and cost associated with the analysis of molecular markers in fine particle samples preclude the potential of analyzing significantly larger numbers of samples. Since some of the health effects studies proposed here require significantly better time resolution measurements than can be achieved by detailed GC/MS analysis, complementary carbon apportionment techniques are worth pursuing. One such approach exploits the thermograms generated by the EC/OC analysis of fine particulate matter that is discussed above. Thermograms generated during the EC/OC analysis of fine particulate matter collected from different air pollution sources using a dilution source sampler demonstrates that the carbonaceous fraction of the fine particulate matter emitted from different air pollution sources can be distinguished with a thermo-evolution analysis. Such observations have been noted in the past by Watson et al. (1994) when analyzing the particulate matter emitted from different types of motor vehicles using an instrument subtly different than the Sunset Laboratory analyzer. It is important to note, however, that the thermograms generated from the analysis of woodsmoke by the Sunset Laboratory instrument are drastically different from the thermograms generated from the analysis of motor vehicle exhaust, food cooking exhaust and many other air pollution sources. To this end, efforts will be pursued to integrate the molecular marker source apportionment results with a more complete analysis of the thermograms generated by the continuous EC/OC analyzer and the lab-based instrument. These results will also be compared to the thermograms generated by the analysis of a broad range of air pollution emission sources with the goal of developing thermogram-based apportionment techniques.

Other Measurements

High-Volume Toxicological Particle Sampler. HSPS will be responsible for a high volume low cut-off inertial impactor (HVLI) to be used to collect large amounts of fine particulate matter for toxicological testing (study #6 in section D.1.2.). The sampler operates at 1100 L/min with a $PM_{2.5}$ inlet upstream from a slit-shaped acceleration jet. The impactor 50% cut-point is 0.12 µm, so overall the sampler collects particles from 0.12 µm to 2.5 µm. No organic vapor denuder is used upstream of the sample collection. The impaction substrate is polyurethane foam (PUF) for the following reasons: (a) PUF has a very high particle collection efficiency over a large range of particle sizes, even under conditions of heavy particle loading, as compared to flat plates and thin porous membranes, which typically are subject to significant bounce-off and re-entrainment; (b) no oil or grease coating is required, so potential interferences of impurities within such coatings are avoided when chemical, biological, and toxicological tests are performed on the collected particles;(c) the PUF itself is chemically inert, minimizing interference with any of these tests; (d) because of the high flow of 1100 L/min, a large amount of particles can be collected in a short period of time, on a relatively small surface of substrate, facilitating recovery of the collected particles for the different tests; and (e) large amounts of particles can be collected on a relatively small collection surface and easily extracted with small amounts of water or organic solvents. This sampler is suitable for the collection of large amounts of particles for toxicological studies and analysis of organic aerosols.

Pollen and Spores. Bioallergen monitoring already conducted in Clayton, MO, will be used to provide a relative index for temporal variations in bioallergen levels at the core and satellite sites. The St. Louis County Department of Health (DOH) operates a National Allergy Bureau (NAB) monitoring site in Clayton. This site is approximately 10 km west of the proposed core site location. Sampling is currently conducted using a Rotorod sampler; however, DOH plans to convert to a Burkard Spore Tap sampler by the end of calendar year 1999. The current schedule provides for weekday sampling only, but we will collaborate with DOH to perform daily sampling during the study period. DOH and/or Washington University staff will service the sampler on the weekends with spore and pollen analysis provided by DOH as in-kind support (a letter of support is presented in Attachment D-II). Washington University will be responsible for processing this data.

Meteorological Measurements. A 30 m meteorological tower will be installed at the core site location or as near as practicable. The following sensors will be located at 30 m and 10 m heights: high-sensitivity sensors for wind speed (cups) and wind direction (tail); temperature and relative humidity sensors in fan-aspirated radiation shields; and solar radiation and barometric pressure sensors. Washington University will be responsible for processing the data, which will be logged as five-minute averages.

Gaseous Criteria Pollutants and Volatile Organic Compounds. The core site will be collocated with the City of St. Louis' Margaretta compliance monitoring station. This will provide additional measurements of criteria pollutants – including gaseous aerosol precursors – to complement the gases measured using the HEADS system. On-site criteria gas pollutant measurements by the City will include: ozone; sulfur dioxide; carbon monoxide; and nitrogen dioxide / nitrogen oxides. U.S. EPA Region VII staff already conducts low-level (60 ppb) audits on the ozone monitor, and will implement a low-level audit program for the sulfur dioxide and nitrogen oxides monitors. Where possible, satellite sites will be selected to coincide with

compliance monitoring sites to provide collocated gaseous pollutant and particulate matter measurements.

There are currently no routine measurements in the St. Louis area for ambient volatile organic compounds. Based on 1997-1999 ozone data, the St. Louis (IL-MO) ozone moderate nonattainment area does not meet the one-hour ozone standard and is subject to reclassification as a serious nonattainment area. If the area is reclassified, Photochemical Assessment Monitoring Stations (PAMS) will be required in St. Louis; if the area is not reclassified, then PAMS will not be required. Regardless of the region's ozone nonattainment status, U.S. EPA Region VII will support PAMS-like monitoring at the core site by providing sampling equipment and performing the chemical analysis. The minimum sampling frequency will be 1-in-6 days, with discussions currently underway to evaluate opportunities for 1-in-3 day sampling.

Single-Particle Analysis

The instrumentation and analysis efforts proposed for the St. Louis Supersite do not explicitly incorporate one of the single-particle analysis instruments that have been recently developed. As these instruments are rapidly improving, it is difficult to assess the ultimate capabilities of each of these instruments over the next few years. It is clear, however, that the long term viability of these instruments relies strongly on the effective integration and calibration of the single-particle analysis instruments with other advanced aerosol characterization techniques. Measurements such as those proposed for the St. Louis Supersite project will provide the means to understand the quantitative response of the single-particle analysis instrument under atmospheric conditions that are relevant to urban air pollution and to human health. For this reason, the St. Louis Supersite Consortium will strongly encourage all of the research groups developing single particle-analysis capabilities to collocate their instruments with the advanced particle matter measurements that are planned at the St. Louis Supersite. The St. Louis Supersite will support such efforts through providing an infrastructure in which the single-particle analysis instruments can be effectively operated and through data sharing. Through these efforts the St. Louis Supersite can make a significant contribution to the development of single particle-analysis technology.

D.2.3. Data Processing, Validation and Interpretation

All data collected as part of this study will be assembled and archived at Washington University for electronic access by all participants. Data management will support the overall study goal by transforming measurement records into reliable and useful information. This goal requires that data access and exploration be facilitated while assured data quality and integrity are maintained. The objective of quick and easy access creates some tension with the objective of assured quality and integrity, but our experience in other large field programs has shown that both can be attained if adequate attention is given to data management.

Data will be centrally managed to forestall the confusion that can arise from ambiguous identification of variables and units or inadvertent use of outdated validation levels. Participants will agree on a common set of variable descriptors and flagging codes, as well as standardized formats for submissions of data to the central archive. Early attention will be given to optimizing these formats to avoid the need for subsequent translation steps that introduce processing delays and possible error. Indicators of validation status and measurement uncertainty will be integrated with data values at the level of individual records, to assure the

retention of this information by individual users. Recorded recipients of early data will be individually notified as new versions emerge from the validation process.

The sustained character of the proposed measurements will be reflected in the near-real-time delivery of as many streams of raw data as are found useful. Data from ongoing measurements have the most value when they are fresh: feedback enables ephemeral auxiliary data to be captured during unusual atmospheric events, and speeds the identification of and attention to instrument anomalies. Feedback also promotes routine inter-variable comparisons by all participants, thereby hastening and strengthening the validation process. Distribution of raw data will be limited to study participants. A mechanism will be developed to release interim (Level 0) data where appropriate. Inappropriate uses will be discouraged by appropriate measures, such as limiting their numerical resolution or providing graphic rather than numeric files.

To promote interpretations that integrate individual measurements within the larger ensemble, the Executive Management Team will issue weekly electronic newsletters during the field program calling attention to noteworthy features in the emerging data. To facilitate such integration, participants will also be provided with routine back-trajectory plots, satellite imagery, and other centrally generated support.

The dynamic and interactive sharing of data and information will be accomplished through a support system based on the world-wide web. This platform will be created and maintained by Drs. Bret Schichtel and Stefan Falke of the Mechanical Engineering Department at Washington University. The website for the St. Louis Supersite will consist of a set of organized forums, for communication among participants and the storage and access of reports and data sets. An example of such a system is the $PM_{2.5}$ analysis workbook website at "http://capita.wustl.edu/PMFine". The ability to submit and discuss resources provides the shared workspace needed for distant groups to work together.

There are a number of organizations producing routine air quality, meteorological and satellite data and making these data available in real time or near-real-time as well as forecasted several days in advance (Table 8). These data provide the local and regional chemical and meteorological context to aid the analysis of data from the Supersite monitors. These supporting data sets will be identified, collected, described and submitted to the Supersite web site on a daily basis to create a data catalog.

A Quality Assurance Project Plan will be prepared to clearly articulate the roles and responsibilities of each investigator regarding data processing, validation, and interpretation. Guidance provided in the NARSTO Quality Systems Management Plan will be followed, and data management will be conducted in accordance with guidance in the NARSTO Data Management Handbook. In general, each investigator will be responsible for data processing of his/her measurement assignments as articulated in section D.2.2. All data will be submitted to the Quality Assurance Officer (Dr. John Watson, DRI) for validation. Subsequently, it will be posted on the website for use by other investigators within the St. Louis Supersite Consortium.

An important part of the data processing and interpretation process will be the selection of the sample subsets to be retrospectively analyzed for trace metals and organic compounds. For trace metals, retrospective analysis will provide 1-hour time resolution for at least twelve elements. For organic compounds, retrospective analysis will provide 24-hour resolution of the component list presented in Table 7. Samples will be selected for retrospective analysis which: (1) represent a range of meteorological conditions; (2) represent a range of $PM_{2.5}$ concentrations,

with emphasis on high $PM_{2.5}$ episodes; (3) for the case of trace elements, capture episodes with high 24-hour integrated concentrations; (4) for the case of organic compounds, capture episodes with low, medium, and high 1-hour and 24-hour integrated organic carbon concentrations determined by EC/OC analysis; and (5) capture the periods when health study intensives and/or single particle analysis studies are being conducted.

D.2.4. Reporting and Dissemination of Results

Reporting and data dissemination mechanisms set forth in the Supersite Terms and Conditions for Award (T&C) - 11/18/99 draft or subsequently adopted version - will be followed. The PI and up to two Co-PIs will attend at least two meetings each year with U.S. EPA to discuss research progress (T&C, part C). Quarterly Progress Reports will be forwarded to the U.S. EPA Project Officer within 30 days after the end of each reporting period. A Final Report will be forwarded to the U.S. EPA Project Officer within 90 days after expiration of the project. The scope and content of these reports will adhere to specifications in T&C parts A and B, respectively.

The web-based information support system described in the previous section will be a key element in disseminating results among investigators and to the outside community. The platform provides for a smooth transition to move data from investigators-only access to public access as deemed appropriate. Dr. John Watson – the QA Officer for this project – will also serve as the designated Data Management Coordinator. He will be responsible for developing a Quality Assurance Project Plan which is consistent with the NARSTO Permanent Data Archive formatting requirements and any additional data delivery agreements negotiated between U.S. EPA and the collective Supersite program awardees. These requirements include the items specified in T&C (part D2) concerning data forwarding to a limited access EPA Supersite Program data web site and a publicly accessible NARSTO Data Archive. Results from this project will be disseminated to the scientific research and policy community via conference presentations and peer-reviewed publications. Appropriate documentation and acknowledgements will be provided as set forth in T&C part D. Finally, a workshop will be held for state and local agencies to provide a conduit for moving the study results into the SIP development process.

D.2.5. Project Participants and Management

Project Management

Figure 7 presents the proposed organizational structure for the St. Louis Supersite. Project management uses a multilayer approach to draw upon the Consortium's highly qualified staff with extensive experience in participating in and managing large research projects. Dr. Jay Turner is the proposed Principal Investigator (PI) who will oversee all administrative and research aspects of this project. He will be assisted by the Executive Management Team of Drs. Judith Chow, Petros Koutrakis, Peter McMurry and Warren White who will share project oversight responsibility with emphasis on their areas of expertise. One-or-more members of the Executive Management Team will be consulted for all substantive decisions regarding the monitoring program scope and content. Furthermore, they will jointly meet with the PI at least quarterly through the first 18 months of the project.

The Internal Steering Committee will consist of all Co-Investigators, additional key personnel, and U.S. EPA staff with substantive collaborative roles. Each investigator has assigned

responsibilities; however, collectively this committee also serves as the forum for working through ideas and shaping the scope and content of the work plan. The primary mode of communication will include regularly-scheduled conference calls and the web-based information support system. The Committee will convene for two data analysis workshops – one following the end of the field campaign and one following completion of the chemical characterizations.

A full-time Field Manager will be hired to handle day-to-day activities at the field sites. This staff person, qualified in operating and maintaining the measurement instrumentation, shall report directly to the PI and will work closely with the investigators responsible for each monitoring package. The operations staff also includes Dr. Judith Chow, who will serve as the Field Operations Advisor. She will work very closely with the Principal Investigator and the Field Manager to address field monitoring logistics. Dr. John Watson will be the Project QA Officer. Dr. Bret Schichtel will be responsible for the web-based information support system.

An External Advisory Committee will be formed to provide input to the Supersites Consortium during the project planning phase. We propose that Dr. Edward Macias of Washington University chair the committee, with the remaining members to be selected in consultation with U.S. EPA. This committee will review and comment on the draft work plan, including a meeting to be convened in St. Louis in Spring 2000.

A Local Government Committee will be formed to facilitate dialogue between the St. Louis Supersite Consortium and local, state and federal air quality officials. The objective is to provide an opportunity for input from these stakeholders during the project planning phase. This committee will review and comment on the draft work plan. A pre-study workshop will be held in Summer 2000 to explore linkages between the field measurement program and state/local needs such as SIP development. A post-study workshop will be convened to disseminate the results.

Technical Qualifications and Responsibilities of the Principal Investigators and Other Key Personnel

Mr. George Allen, Supervising Engineer at Harvard School of Public Health, will be responsible for the Harvard University-based instrumentation packages and laboratory analysis. Mr. Allen has more than fifteen years experience in environmental monitoring and method development, and has managed a large number of air pollution field studies in the United States and abroad. Mr. Allen will be the project manager for the HSPH components, and will be responsible for deployment and operational oversight of the continuous and integrated measurement methods provided by HSPH.

Dr. Tina Bahadori, Manager of Air Quality Health Integrated Programs within the Environment Group at EPRI, will provide expertise in project management and support. In her capacity at EPRI, she is responsible for research related to the health effects of air pollution. She is currently managing several projects which examine the composition and characteristics of aerosols in different geographic regions and evaluate the potential population exposure and health effects. These projects include the Aerosol Research Inhalation Epidemiology Study (ARIES) in Atlanta, as well as the Midwest Aerosol Research Characterization Study (MARCH-MW).

Dr. Judith Chow, a Research Professor at the Desert Research Institute (DRI), will serve on the Executive Management Team and as the Field Operations Advisor. She will participate in project planning and design of the measurement platforms, conduct visits, and perform

retrieval/reformatting/processing tasks. Dr. Chow will oversee the quality assurance activities to be conducted for this project, and will evaluate the data analysis plan to assure the study objectives are met. Dr. Chow has over 23 years of experience in conducting air quality studies and performing statistical data analysis. She currently directs DRI's Environmental Analysis Facility. Dr. Chow is the principal author or co-author of more than 100 peer-reviewed publications and more than 150 technical reports. She is a member of the National Academy of Sciences/National Research Council's Committee on Research Priorities. She was invited to present and publish the Air & Waste Management Association's 1995 annual critical review on aerosol measurement methods. Dr. Chow has been principal investigator or a major collaborator in more than 40 large air quality studies and many smaller ones.

Dr. Petros Koutrakis, Professor of Environmental Sciences and the Director of the Environmental Chemistry Laboratory at the Harvard School of Public Health, will serve on the Executive Management Team. He will work closely with the Principal Investigator on study design and data analysis issues. Also, because he is the PI or Co-PI for most of the exposure and health effects studies, he will be responsible for the coordination of the Supersite program and those studies. Dr. Koutrakis is the Technical Editor-in-Chief of the *Journal of the Air and Waste Management Association*. Also, he is the director of the EPA/Harvard Particle Center. He has authored more than 80 peer-reviewed publications in the fields of methods development, environmental chemistry, aerosol engineering and source apportionment. He holds four U.S. patents for monitoring methods and instrumentation. Dr. Koutrakis supervises a group of more than twenty-five scientists and over the last twelve years he has been the Principal Investigator of more than twenty projects. Currently, he is a member of the National Research Council Panel on Ambient Particle Health Effects and member of the Clean Air Scientific Advisory Subcommittee to review the PM NAAQS. Also, he is the chairman of the EPA Speciation Network Panel.

Dr. Peter H. McMurry, Head of the Department of Mechanical Engineering at the University of Minnesota, will be responsible for measurements of aerosol size distributions and integral moments of physical properties. He will also work closely with the Principal Investigator as a member of the Executive Management Team, focusing on aerosol science issues. Dr. McMurry has been a regular participant in atmospheric field studies since 1977. This field research includes studies of pollution aerosols in locations including Los Angeles, Atlanta, the Grand Canyon, and the Great Smoky Mountains as well as studies of remote troposphere aerosols at locations ranging from the North Pole to Mauna Loa, Tasmania and the South Pole. He has published more than 100 peer-reviewed journal articles, and was recently invited by NARSTO to write an extensive review of atmospheric aerosol physical property measurements which will appear shortly in Atmospheric Environment.

Dr. Edward Macias, Professor of Chemistry and Dean of Arts and Sciences at Washington University in St. Louis, will Chair the External Advisory Committee. Dr. Macias has studied ambient aerosols for over 20 years, participating in major field studies, the development of field instrumentation and nuclear analytical techniques, and data interpretation. He has worked extensively on the scientific basis of visibility, particularly in the Western U.S.

Dr. John Ondov, Professor of Chemistry at the University of Maryland, will oversee the construction, field deployment, and operation of the HFASS trace element analysis sampler. He will also take a lead role on study design issues and data analysis regarding trace elements chemical characterization and source apportionment. Dr. Ondov has 24 years experience in the

conduct of multidisciplinary projects for the U.S. DOE, Martin Marietta Corporation, and the University of Maryland. He is the PI of the EPA STAR Grant which funded development of the SEAS monitor to be used in this study. Previously, Dr. Ondov developed one of the first and most widely used CMB profiles for automobiles, developed a unique methodology for apportioning fugitive emissions from industrial plants to specific processes, and pioneered the development of extremely sensitive enriched rare-earth isotopic tracer techniques for use in source attribution and studies of aerosol particles over transport distances of hundreds of kilometers. He has conducted several receptor modeling studies using intentional tracers and tracers of opportunity.

Dr. James Schauer, Assistant Professor of Civil and Environmental Engineering at the University of Wisconsin-Madison and the Director of Air Chemistry at the Wisconsin State Laboratory of Hygiene, will provide the leadership and expertise for the collection and analysis of particle-phase organic compounds. He will also be responsible for the continuous and integrated measurements of particle-phase organic and elemental carbon for the project. Dr. Schauer has extensive experience in the measurement of emissions from air pollution sources and the detailed chemical analysis of particle-phase organic compounds present in atmospheric samples and in source emissions. The molecular marker source apportionment techniques developed by Dr. Schauer and his colleagues provide the basis for the organic compound speciation efforts planned by the U.S. EPA for the Fine Particle Chemical Speciation Network. Dr. Schauer has served as a consultant for the U.S. EPA's Emissions Characterization & Prevention Branch to develop a source-testing program and a chemical analysis program that will support molecular marker source apportionment efforts.

Dr. Bret Schichtel, Senior Research Associate at Washington University in St. Louis, will be responsible for the web-based information support system. He will oversee and participate in the implementation of the website and the addition of meteorological, satellite and regional and local air quality data resources. Dr. Schichtel has extensive experience in providing web based support to the air quality research and management communities involved in large projects to facilitate communication, cooperation and sharing of resources among the participants and others. Past projects have included the establishment of websites and collection of data resources in support of the Ozone Transport Assessment Group (OTAG) Air Quality Analysis Workgroup and the tracking and analysis of a China dust plume and smoke from Central American fires that impacted the United States during the spring of 1998. Currently, he is overseeing the "PM Fine" analysis website which was developed to support EPA's Virtual Workgroup for the $PM_{2.5}$ Analysis Workbook.

Dr. Jay Turner, Assistant Professor at Washington University in St. Louis with a joint appointment in the Department of Engineering & Policy and Department of Chemical Engineering, will be the Principal Investigator for this project. With the guidance of the Executive Management Team, he will carry out the tasks related to overall project administration, execution, and reporting. Dr. Turner has conducted several field studies to characterize particulate matter emissions and ambient burdens. Selected ongoing projects include: a laboratory and field characterization of particulate matter sampling devices; field studies to quantify motor vehicle particulate matter emissions, with emphasis on road dust and tire wear; field studies to quantify biogenic volatile organic compound emissions from oak forests; and saturation monitoring for fine particulate matter in the St. Louis airshed. He has authored fourteen publications in peer-reviewed journals and one book chapter. Nationally, he

served on the Science and Technical Support Work Group of the FACA Subcommittee for Ozone, Particulate Matter and Regional Haze Implementation Programs.

Dr John Watson, Research Professor at DRI, will serve as DRI's Senior Technical Advisor and Quality Assurance Officer. A summary of his responsibilities is presented in the Quality Assurance Narrative Statement of this proposal. Dr. Watson is a nationally and internationally recognized expert on $PM_{2.5}$ special studies including network design, sampling, analysis, database management, and modeling. He has over 25 years of experience in the environmental sciences, including the conduct and management of air quality studies, and has more than 100 publications in the fields of physics, source/receptor modeling, and air quality measurement and analysis. Dr. Watson has been instrumental in advising U.S. EPA and preparing U.S. EPA guidance documents on such topics as network design, continuous instruments, and chemical speciation for $PM_{2.5}$. Dr. Watson has designed dozens of major aerosol characterization studies, including $PM_{2.5}$, and developed the EPA/DRI Chemical Mass Balance (CMB) source/receptor model, which has been applied in many urban areas for the development of state implementation plans. He is currently planning the design and implementation of the California Regional $PM_{10}/PM_{2.5}$ Air Quality Study (CRPAQS).

Dr. Warren White, Senior Research Associate at Washington University in St. Louis, will work closely with the Principal Investigator on study design issues, data integration, data analysis, and report preparation. Dr. White worked on the 1972-73 Aerosol Characterization Experiment (ACHEX) in Los Angeles, for which he developed the now-familiar concept of the light-extinction budget. He was subsequently co-PI on the 1974-76 Midwest Interstate Sulfur Transformation and Transport (MISTT) study in St. Louis, which documented with unprecedented clarity the long-range impact of urban emissions. Since coming to Washington University in 1979 Dr. White has continued to work on ambient aerosols, their effects on the atmosphere, and their relationship to particle and precursor gas emissions. In the last 15 years he has focused particularly on characterizing uncertainties in particle measurements, their interpretation, and modeling, authoring about 40 peer-reviewed technical papers in this area. Dr. White currently serves on the Clean Air Science Advisory Committee (CASAC), the audit team for the Epidemiology Reanalysis Project of the Health Effects Institute (HEI), and National Research Council committees for assessment of the North American Research Strategy for Tropospheric Ozone and Research Priorities for Airborne Particulate Matter.

D.2.6 Facilities and Resources

All of the participating institutions have the infrastructure to execute their responsibilities to this project. Furthermore, facilities are available at many institutions to perform a given analysis, providing the project with a high degree of flexibility. However, for brevity this section shall highlight each institution's facilities and resources commensurate to their responsibilities articulated in the proposal.

Desert Research Institute. The Environmental Analysis Facility (EAF) at DRI will be used for routine analysis of filter samples and denuders for ions and absorbed gaseous species. DRI will also perform XRF analysis for the intercomparison of trace element analysis methods. EAF was established in 1985 and is led by Dr. Judith Chow. It is an inorganic chemistry research and testing laboratory that has been especially constructed and equipped to perform chemical speciation of atmospheric contaminants (trace elements, ions, and carbon) collected on filter substrates. Aerosol and gas sampling substrates are prepared in a temperature- and humidity-

controlled filter processing clean room without contamination. Of particular relevance to this project are the following instruments: a Technicon Random Access Automatic Colorimetry System (TRAACS 800) for soluble ion analysis; a Dionex 500DX dual channel ion chromatograph (IC) for soluble ion analysis; and two Kevex 0700/8000 energy dispersive x-ray fluorescence (EDXRF) analyzers for non-destructive elemental analysis. Additional instrumentation includes microbalances, atomic absorption spectrometers, and thermal/optical carbon analyzers. An inductively coupled plasma-mass spectrophotometer (ICP-MS) is also available at DRI.

DRI's organic analysis laboratory (OAL), established in 1991 and led by Dr. Barbara Zielinska, specializes in sampling and speciation of a wide range of volatile, semi-volatile, and particulate organic compounds. OAL is a fully instrumented facility for organics analysis; in this project, GC-MS will be used for the QA laboratory intercomparison for organic speciation.

Harvard University School of Public Health. The Environmental Chemistry Laboratory at HSPS will provide support for most of the continuous particle mass and speciation monitors. They will condition denuders and perform gravimetric analysis. Instruments available for the analysis of particle samples include GC/MS for organics, Plasma Emission Spectroscopy for elements, HPLC for particulate-phase polycyclic aromatic hydrocarbons, a pH-meter for aerosol acidity, and IC for ions. Gravimetric analysis of the particulate matter collected on filters will be performed in a temperature and relative humidity controlled room. Equipment for personal measurements, microenvironmental and outdoor measurements is available.

University of Maryland at College Park. UMCP will construct a HFASS unit for collecting 1-hour average samples suitable for elemental analysis. They will retrospectively analyze a subset of these samples at the UMCP facilities. GRAAZ and INAA will be used for elemental analysis as part of the methods intercomparison. Available facilities include a Nuclear Analysis Laboratory (120 m^2), a cold-room (-4°C) for sample storage, a 120 m^2 Class 100 Clean Room complex, a 110 m^2 aerosol measurements laboratory, and a newly-renovated 39-m^2 clean chemistry laboratory for performing contaminant-free sample preparations and packaging. Neutron irradiations for INAA analysis are performed at the National Institute for Standards and Technology (NIST) in Gaithersburg, MD. Counting facilities are maintained at NIST and UMCP for measuring short- and long-lived activation products, respectively. Atomic spectroscopy for this project will be conducted using a Perkin Elmer SIMMA 6000 simultaneous multielement Electrothermal Atomic Absorption Spectrometer with Zeeman background correction (ETAA-Z).

University of Minnesota. The Particle Technology Laboratory (PTL) at the University of Minnesota will calibrate and maintain the aerosol size distribution and integral moments instruments. PTL is based in the Department of Mechanical Engineering at the University of Minnesota, and was founded by the late Professor Kenneth T. Whitby about 40 years ago. Research activities of five faculty members including Dr. McMurry are exclusively housed in this laboratory. Research conducted by PTL covers a broad spectrum of topics that involve the measurement and behavior of gas-borne particles. The laboratory is equipped with state-of-the-art instrumentation for ensuring and generating aerosols ranging from <3 nm to 100 µm, and this equipment will be available to this project. Many instruments that are used worldwide for aerosol measurement have been developed wholly or in part by researchers at the PTL.

University of Wisconsin-Madison. The Wisconsin State Laboratory of Hygiene (WSLH) will be used as the analytical facility for the measurement of fine particle organic compounds, the elemental and organic carbon (EC/OC) measurements, and the measurement of fine particle trace metals by ICPMS. The WSLH operates as part of the University of Wisconsin-Madison and has enjoyed long standing collaborative relationships with the academic departments of the University. The success of these collaborations is in part due to the senior staff of the WSLH, who hold tenured and tenure-track academic positions within the academic departments of the University. As an example, Dr. James Schauer is a faculty member of the UW-Madison Civil and Environmental Engineering Department and is the Director of Air Chemistry at the WSLH.

WSLH is a fully accredited and certified environmental and occupational exposure-testing laboratory, and routinely performs a full range of EPA and OSHA analytical methods. WSLH maintains dedicated equipment for the analysis of semi-volatile and particle-phase organic compounds present in air pollution samples. The dedicated equipment includes solvent extraction equipment, extract concentration and derivatization equipment, and a HP5973 GC/MS. The University of Wisconsin-Madison will use a VG PlasmaQuad II+ ICPMS running with Maglev turbo pumps and a high performance interface for the ICPMS analysis of fine particle trace metals. When operated with pneumatic aspiration, the instrument will give 20-30 million counts per ppm of a mono-isotopic element. The sensitivity is further increased 5 to 15 fold, depending upon the isotope, when interfaced with our ultrasonic nebulizer (CETAC 5100AT). The ICP-MS lab also operates a state-of-the-art microconcentric nebulizer (CETAC MCN-6000) which exhibits many of the superior sensitivity and polyatomic removal characteristics of the ultrasonic nebulizer, yet consumes less than 100 µL of sample per minute. The very low sample consumption rate is also ideal for limited volume aerosol digestates. Wetted components of the MCN-6000 are constructed entirely of inert Teflon, ideal for the aggressive acids used in the aggressive solubilization process of extracting trace metals from airborne particulate matter.

The ICP-MS is sited in a dedicated metals clean room at the Wisconsin State Lab of Hygiene. UW-Madison investigators have over a decade of experience in trace element analysis and process studies of environmental systems, and have pioneered many of the techniques now used by university, state, and federal agencies for trace metal sampling and analysis (Shafer et al. 1998; Shafer et al. 1997; Hurley et al. 1996).

Washington University. Staff from the Air Quality Laboratory (AQL) at Washington University will be responsible for the day-to-day operation of the core and satellite sites. The laboratory is equipped to serve as a staging area for preparing substrates. A dedicated laminar flow hood is available for clean substrate and sample handling. AQL is also equipped for sample processing, including extraction apparatus and rotary evaporators in support of handling denuders. Freezer storage for large volumes of samples will be provided. AQL occupies 650 ft^2 of laboratory space exclusively to support its field activities, with analytical equipment housed at a separate, shared facility. Washington University will also provide a robust infrastructure for data storage and back-up, including the handling of raw data from the continuous samplers.

D.2.7. Research Collaboration with U.S. EPA Scientists

The St. Louis-Midwest Supersite consortium will collaborate with U.S. EPA scientists on a range of research issues. While the precise nature and scope of such collaborations is evolving, initial discussions with U.S. EPA scientists have identified the following potential opportunities.

- *External Advisory Committee*. This committee will consist of U.S. EPA and other scientists and will be staffed during the first quarter of the project. In addition to the named scientists below, we have discussed this opportunity with Dr. Marc Pitchford (Office of Air Quality Planning and Standards) and Dr. Paul Solomon (National Exposure Research Laboratory).
- *Dr. Kevin Dreher – Pulmonary Cell Biology and Molecular Toxicology Group, National Health and Environmental Effects Research Laboratory*. Results from in vivo and in vitro toxicology studies have identified a large number of potential causal properties of ambient air particulate matter health effects. The list of potential particulate matter causal properties include particle acidity, bioaerosols, inorganic and inorganic constituents as well as particle physical properties such as size, surface area and number. Research is critically needed to evaluate the "coherence" of these potential causal particulate matter properties with the adverse health effects associated with air particulate pollution exposure. The St. Louis Supersite can address the issue of "coherence" of causal particulate matter properties by providing to health effects scientists, at the National Health and Environmental Effects Research Laboratory of the U.S. EPA, ambient air particulate matter samples collected during periods of particulate matter epidemiology studies. U.S. EPA health effects scientists will evaluate the physicochemistry and toxicity of the collected particulate matter samples using analyses that are appropriate for the amount of particulate matter collected. Information obtained from the physicochemistry and toxicology studies will be correlated with the epidemiology in order to evaluate the coherence of specific particulate matter properties with identified adverse particulate matter-associated health effects.
- *Dr. Dean Smith – Air Pollution Prevention and Control Division, National Risk Management Research Laboratory*. Dr. Smith is heading up a source testing program with the U.S. EPA's ORD to obtain source profiles that can be used in fine particle air pollution models including the molecular marker source apportionment model developed at Caltech by Schauer et al. (1996). Dr. Smith's group is currently working with Prof. James Schauer – a Co-PI for the proposed St. Louis Supersite – on the development of an inter-laboratory comparison program for the analysis of organic compounds in atmospheric particulate matter samples and source emissions samples. In addition, Dr. Smith is working with Prof. Schauer's research group on a particulate matter metals analysis intercomparison study to compare the University of Wisconsin's advanced ICP-MS capabilities with the U.S. EPA XRF analysis. Potential collaboration between the Dr. Smith's group and the St. Louis Supersite program include: (a) providing input to U.S. EPA on prioritization of air pollution sources to test as part of U.S. EPA source testing program; (b) U.S. EPA testing of air pollution sources important to St. Louis that have not been previously tested; (c) U.S. EPA participation in the Supersite metals analysis intercomparison study with the use of the U.S. EPA's XRF analysis capabilities; (d) an intercomparison between UW-Madison and U.S. EPA for the analysis of organic compounds present in fine particulate matter samples and the measurement of fine particulate matter elemental and organic carbon (ECOC); and (e) U.S. EPA analysis by SEM of selected ambient samples collected in St. Louis.
- *Dr. William Wilson – National Center for Environmental Assessment.* Dr. Wilson was the Project Officer for MISTT, the program to map St. Louis emissions by instrumented aircraft in conjunction with RAPS during the summers of 1974-1976. Dr. Wilson and Washington University investigators have collaborated since then on several analyses of MISTT data, and plan to integrate the historical data from RAPS into the interpretation of Supersite results. A variety of other opportunities for collaboration are being explored with Dr. Wilson, including:

(a) measurement of semivolatile compounds, for which Dr. Wilson is currently collaborating in a cooperative agreement with Dr. D. Eatough and Dr. P. Hopke in the measurement of total (non-volatile and semivolatile) particulate matter and can encourage them to make some measurements in St. Louis; (b) interpretation of the St. Louis Supersite integral moments measurement data and PM_1 mass concentration data, with emphasis on spatial variability and applications as exposure surrogates for health studies; and (c) investigations of the climatology of aerosol size distributions.

- *Dr. Donna Kenski – U.S. EPA Region V.* Dr. Kenski has significant experience in the receptor modeling and the data validation of VOC measurements. She will work with the St. Louis team to validate the VOC data.
- *Mr. Michael Davis and Mr. Joshua Tapp, U.S. EPA Region VII.* As described in Section D.2.2. (page D-22), U.S. EPA Region VII staff will provide low-concentration audits for the criteria gas monitors and will support VOC measurements by providing sampling hardware and performing sample analysis. Furthermore, we are pursuing extensive coordination and collaboration between the St. Louis Supersite program and U.S. EPA Region VII's risk-based air screening analysis project (described on page D-18) to be conducted in St. Louis under the Community Based Environmental Partnership (CBEP) program. Current plans for the CBEP project include at least one year of monitoring for about thirty-two air toxic compounds. The proposed air toxics monitoring site is located in the City of St. Louis approximately 6 km south of our proposed core monitoring site. While the draft work plan for the risk-based air screening analysis project is still being developed, several areas for potential collaboration have been discussed including: (a) siting of the University of Maryland HFASS sampler at the air toxics site for a portion of 4th Quarter 2000 subject to funding for sample analysis (the air toxics monitoring program will likely run October 2000 through September 2001, while the full suite of Supersite measurements commencing in January 2001); (b) conducting a data intercomparison for any species measured at both the air toxics and Supersite sites (current plans would yield nine months of overlapping measurements, January-September 2001); (c) investigate broader data integration between these two efforts as most of the measurements are complementary rather than directly overlapping (for example, the Supersite time-resolved trace elements data will be valuable information for the air toxics project); and (d) incorporate data obtained from air toxics monitoring into the selection process for retrospective speciation analysis of 24-hour average samples for organic compounds and 1-hour average samples for trace elements, to the mutual benefit of both the Supersite and CBEP program objectives.

In addition, preliminary discussions with Dr. Jason Ching (National Exposure Research Laboratory) focused on using the St. Louis Supersite measurements for an operational evaluation of forthcoming neighborhood scale modeling using Models3. It is recognized that this collaboration would require additional resources to support enhanced meteorological measurements in St. Louis. Discussion with these and other U.S. EPA scientists will be pursued during the first quarter of the project where the effort is targeted towards refining the project work plan. Per conversations with Dr. Paul Solomon, there also may exist opportunities for collaboration with postdoctoral researchers at U.S. EPA.

D.2.8. Schedule

The performance period for this four year project is January 1, 2000 through December 31, 2003. Calendar year 2000 activities focus on project planning, site preparation, and equipment

installation. Sampling equipment will be phased into operation over the period October-December 2000. Calendar year 2001 will be the 12 month continuous sampling campaign, starting in January 2001 and ending in December 2001. Calendar year 2002 will focus on chemical characterization and preliminary data analysis. Retrospective analysis for trace metals speciation and organic compound speciation will follow after chemical characterization of the particle speciation network-type samples. Finally, calendar year 2003 tasks include additional data analysis and interpretation with emphasis on collaborative analyses between researchers. The proposed project schedule is summarized in Table 9.

ATTACHMENT D-I: TABLES AND FIGURES

Table 1. Historical particle concentrations in St. Louis: annual averages for 1976 over the 10-station RAPS network.

Parameter	PM_{20} ($\mu g/m^3$)	$PM_{2.4}$ ($\mu g/m^3$)
mass	42	21
S	2.9	2.6
Si	3.5	0.3
Al	1.0	0.15
Ca	2.2	0.06
Pb	0.6	0.5
V	0.005	0.003
Ti	0.2	0.03
Fe	1.0	0.2

Table 2. Historical particle concentrations in St. Louis City: annual averages for 1980-1986 from Six Cities monitor in Carondolet.

Year	$PM_{2.5}$ ($\mu g/m^3$)
1980	22.0
1981	19.5
1982	17.7
1983	17.3
1984	18.4
1985	17.7
1986	17.9

Table 3. Historical particle concentrations in St. Louis County: annual mean of quarterly averages for 1988-1997 in Clayton.

Year	$PM_{2.5}$ ($\mu g/m^3$)	Comments
1988	15.0	Q_3 and Q_4 only
1989	17.4	
1990	10.3	Q_1, Q_2 and Q_4 only
1991	14.5	
1992	14.3	
1993	15.9	
1994	14.0	Q_4 only
1995	16.4	
1996	15.1	
1997	14.9	Q_1, Q_2 and Q_3 only

Table 4a. Proposed measurements for the St. Louis Supersite - aerosol physical properties.[1]

***In Situ* Measurements (Continuous or Semi-Continuous Automated Measurements)**				
	Size Range	***Duration***	***Core***	***Satellite***
Aerosol Size Distribution				
Nano-Scanning Mobility Particle Spectrometer (SMPS) (University of Minnesota)	3-20 nm	5 min	X	
Scanning Mobility Particle Spectrometer (SMPS) (University of Minnesota)	20-500 nm	5 min	X	
LasAir Optical Particle Counter (University of Minnesota)	0.2-2 µm	5 min	X	
Aerodynamic Particle Sizer (University of Minnesota)	0.3-10 µm	5 min	X	
Integral Moments of Physical Aerosol Properties				
Number Concentration (TSI 3025 Ultrafine CPC) (University of Minnesota)	>3 nm	2 sec	X	X
"Dry" Light Scattering Coefficient (Nephelometer) (University of Minnesota)	<2.5 µm	2 sec	X	X
Electrical Charge Integral (University of Minnesota)	<2.5 µm	2 sec	X	X
Transmittance through filter deposits (Aethalometer) (Harvard University)	<2.5 µm	5 min	X	X
Total Mass Concentration (CAMMS) (Harvard University)	<2.5 µm	1 hour	X	X

Substrate Methods (Time-Integrated Manually-Operated Samplers)				
Particle Mass Concentration	***Size Range***	***Duration***	***Core***	***Satellite***
Harvard Impactor (Harvard University)				
- PM_1	<1.0 µm	24 h	X	X
- $PM_{2.5}$	<2.5 µm	24 h	X	X
- PM_{10}	<10 µm	24 h	X	X
HEADS (Harvard University)				
- $PM_{2.5}$	<2.5 µm	24 h	X	X
Sequential FRM (City of St. Louis)				
- $PM_{2.5}$	<2.5 µm	24 h	X	(X)[2]
Non-Sequential FRM (City of St. Louis)				
- PM_{10}	<10 µm	24 h (1-in-6 days)	X	(X)[2]
High Resolution Dichotomous Sampler (Harvard University)				
- fine PM ($PM_{2.5}$)	<2.5 µm	24 h	X	X
- coarse PM ($PM_{10} - PM_{2.5}$)	2.5-10 µm	24 h	X	X

Table 4b. Proposed measurements for the St. Louis Supersite - aerosol chemical properties.[1]

***In Situ* Measurements (Semi-Continuous Automated Measurements)**				
	Size Range	***Duration***	***Core***	***Satellite***
Sulfate (e.g., R&P/ADI, HSPH, ARA) (Harvard University)	<2.5 µm	10 min	X	X
Nitrate (e.g., R&P/ADI, HSPH, ARA) (Harvard University)	< 2.5 µm	10 min	X	X
OC/EC (Sunset Laboratory Instrument) (University of Wisconsin)	<2.5 µm	1 hour	X	

Substrate Methods (Time-Integrated Manually-Operated Samplers)				
	Size Range	***Duration***	***Core***	***Satellite***
HEADS: sulfate, nitrate, ammonium, potassium and sodium ions, acidity, ammonia, nitric/nitrous acid, SO_2 (Harvard University)	<2.5 µm	24 hour	X	X
OC/EC (NIOSH method 5040) (University of Wisconsin)	<2.5 µm	24 hour	X	X
Trace Metals (analytical method to be determined)	<2.5 µm	24 hour	X	X
Coarse PM Trace Metals[3] (analytical method to be determined)	<10 µm - or - 2.5-10 µm	24 hour	X	X
12^+ elements (from As, Cu, Mn, Ni, Cr, Cd, Se, Ag, Pb, Al, Fe, Zn, Ca, V, Ti, Be, Ba) (HFASS-GRAAZ) (University of Maryland)	<2.5 µm	1 hour (retrospective analysis @ ~1200 samples)	X	
Organic compound speciation (University of Wisconsin)	<2.5 µm	24 hour (retrospective analysis @ ~110 samples)	X	
Toxicological sampling (1630 m^3 sampling volume) (Harvard University)	<2.5 µm	1 week (retrospective analysis)	X	

Table 4c. Proposed measurements for the St. Louis Supersite – other measurements.[1]

		Duration	***Core***	***Satellite***
Airborne Bioallergens (St. Louis County and Washington University)		24 hour	Clayton, MO	
Meteorological Parameters (Washington University) - wind speed - wind direction - temperature - relative humidity - barometric pressure - solar radiation		5 min	X	
Criteria Gas Pollutants (City of St. Louis) - nitric oxide / nitrogen oxides - ozone - carbon monoxide - sulfur dioxide		1 hour	X	(X)[1]

FOOTNOTES:

(1) All measurements will be sustained for an entire year. Thus, the sampling frequency is the reciprocal of the duration (e.g., 24 hour samples will be collected 1/day, hourly samples will be collected 24/day) unless other noted.

(2) Criteria gaseous pollutants, $PM_{2.5}$ and PM_{10} will be available at satellite sites collocated with compliance network monitors. Responsible agencies include the City of St. Louis, St. Louis County, Missouri Department of Natural Resources, and Illinois Environmental Protection Agency.

(3) Analysis of either PM_{10} samples or dichotomous sampler coarse filter samples.

Table 5. HEADS performance for gases and particulate matter ions.

Measurement Parameter	Precision (Std. Dev.)	Accuracy	Completeness
H^+	< ±15%	< ±15%	95%
SO_4^{2-}	< ±10%	< ±15%	95%
NO_3^-	< ±20%	< ±20%	95%
NH_4^+	< ±20%	< ±20%	95%
HNO_2	< ±20%	< ±20%	95%
HNO_3	< ±20%	< ±20%	95%
SO_2	< ±10%	< ±15%	95%

Table 6. Estimated detection factors for GFAA with dynamic aerosol preconcentration (DAP).

	ambient air concentration[1], ng/m³		method detection limit, pg	detection factor	
element	$[C_i]_{average}$	$[C_i]_{minimum}$		for $[C_i]_{average}$	for $[C_i]_{minimum}$
Ag	0.059	0.006	1	12	12
Al	121	24.8	6	827	4,033
As	0.69	0.337	10	67	138
Cd	0.131	0.0119	0.4	60	655
Co	0.159	0.051	8	13	40
Cr	0.79	0.039	1.6	49	988
Cu	2.35	0.31	5	16	118
Fe	117	33	6	165	585
Mn	3.09	0.05	1.8	5	309
Mo	0.712	0.057	4	3	36
Ni	2.92	0.36	16	45	365
Pb	4.13	0.316	3	6	75
Sb	0.495	0.185	8	5	12
Se	1.53	0.592	8	148	383
Ti	12	0.017	10	1.7	1,200
V	3.24	0.564	18	63	360
Zn	13.5	4.7	6	1,567	4,500

(1) Reported by Wu et al., 1994.

Table 7. Organic compounds in 24-hour integrated $PM_{2.5}$ samples to be quantified by GC-MS.

Alkanes	Resin Acids	PAH
Tetracosane	Pimaric acid	Fluoranthene
Pentacosane	Isopimaric acid	Acephenathrylene
Hexacosane	Sandaracopimaric acid	Pyrene
Heptacosane	8,15-Pimaredienoic acid	Methyl substituted MW 202 PAH
Octacosane	Dehydroabietic acid	Benzo[ghi]fluoranthene
Nonacosane	7-Oxodehydroabietic acid	Cyclopenta[cd]pyrene
Triacontane	Abieta-6,8,11,13,15-pentae-18-oic acid	Benz[a]anthracene
Hentriacontane	Abieta-8,11,13,15-tetraen-18-oic acid	Chrysene/Triphenylene
Dotriacontane	Abietic acid	Methyl substituted MW 226 PAH
Tricontane		Methyl substituted MW 228 PAH
Tetracontane	Aromatic Acids	Benzo[k]fluoranthene
Pentacontane	1,2-Benzenedicarboxylic acid	Benzo[b]fluoranthene
Hexacontane	1,3-Benzenedicarboxylic acid	Benzo[j]fluoranthene
	1,4-Benzenedicarboxylic acid	Benzo[e]pyrene
Branched Alkanes	4-Methyl, 1,2-Benzenedicarboxylic acid	Benzo[a]pyrene
iso-Nonacosane	Benzenetricarboxylic acids	Perylene
anteiso-Triacontane	Benzenetetracarboxylic acid	Indeno[cd]fluoranthene
iso-Hentriacontane		Indeno[cd]pyrene
anteiso-Dotriacontane	Alkanedioic acids	Benzo[ghi]perylene
iso-Tricontane	Propanedioic acid	Coronene
	Butanedioic acid	Retene
Saturated Cycloalkanes	Methylpropanedioic acid	
Pentadecylcyclohexane	Methylbutanedioic acid	Oxy-PAH
Hexadecylcyclohexane	Pentanedioic acid	Anthracen-9,10-dione
Octadecylcyclohexane	Hexanedioic acid	1H-Phenalen-1-one
Nonadecylcyclohexane	Heptanedioic acid	Benz[de]anthracen-7-one
	Octanedioic acid	Benz[a]anthracen-7,12-dione
Alkanoic Acids	Nonanedioic acid	1,8-Naphthalic anhydride
Tetradecanoic acid		Benzo[cd]pyren-6-one
Pentadecanoic acid	Hopanes	
Hexadecanoic acid	22,29,30-Trisnorhopane	Substituted Phenols
Heptadecanoic acid	17a(H)-21b(H)-29-Norhopane	Coniferyl aldehyde
Nonadecanoic acid	18a(H)-29-Norneohopane	Propenylsyringol
Eicosanoic acid	17a(H)-21b(H)-Hopane	Syringealdehyde
Heneicosanoic acid	22R&S,17a(H),21b(H)-30-Homohopane	Acetosyringone
Docosanoic acid	22R&S,17a(H)21b(H)-30-Bishomohopane	Acetonylsyringol
Tricosanoic acid		Propionylsyringol
Tetracosanoic acid	Steranes	Butyrylsyringol
Pentacosanoic acid	20R,5a(H),14b(H),17b(H)-Cholestane	Sinapic aldehyde
Hexacosanoic acid	20S,5a(H),14b(H),17b(H)-Cholestane	
Heptacosanoic acid	20R,5a(H),14a(H),17a(H)-Cholestane	Other Compounds
Octacosanoic acid	20R,5a(H),14b(H),17b(H)-Ergostane	Levoglucosan
Nonacosanoic acid	20S,5a(H),14b(H),17b(H)-Ergostane	Cholesterol
Triacontanoic acid	22R,5a(H),14b(H),17b(H)-Sitostane	Bis(2-ethylhexyl)phthalate
	22S,5a(H),14b(H),17b(H)-Sitostane	Dibutylphthalate
Alkenoic acids		Dimethylphthalate
9-Hexadecenoic acid		Dihydroxynitrobenzene
9-Octadecenoic acid		Dibenzofuran
9,12-Octadecanedienoic acid		Squalene

Table 8. A sample of the available secondary data to be integrated into the St. Louis Supersite web site.

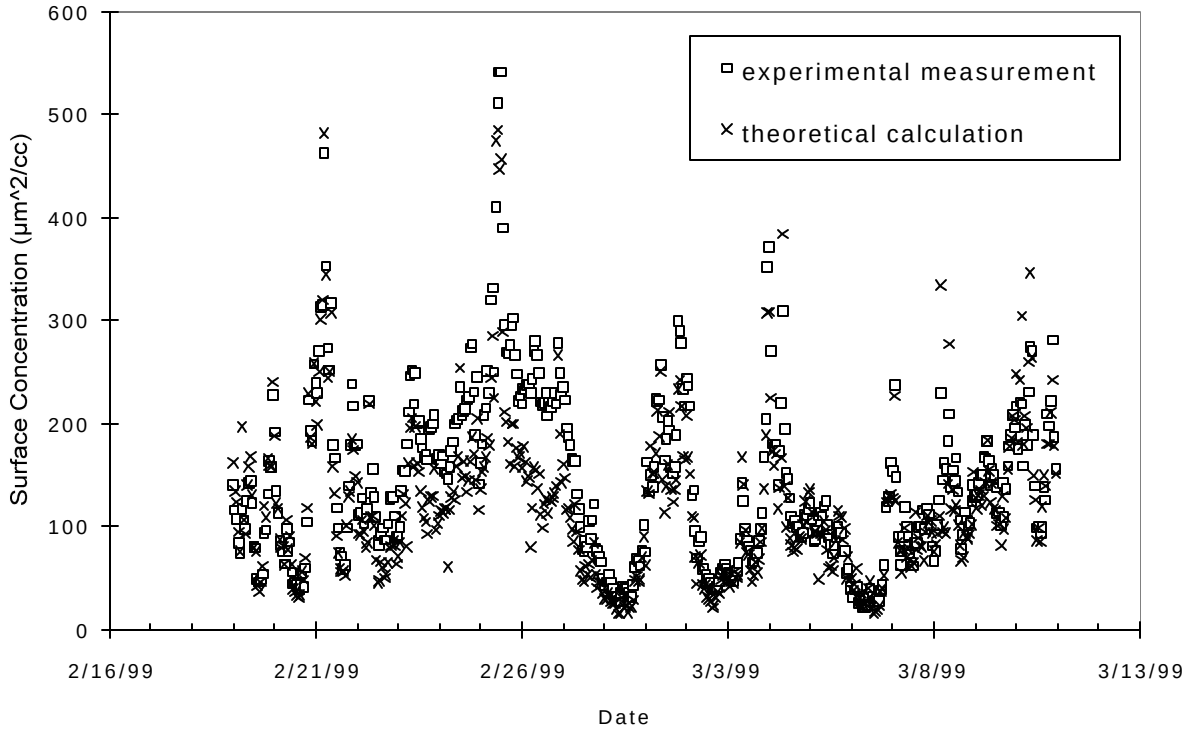
Type	Source	Location & Parameters	Availability
Local Air Quality	Missouri DNR http://www.dnr.state.mo.us/deq/esp/esp_aqm.htm	Missouri criteria pollutants	Hourly
Regional Air Quality	AIRNOW http://www.epa.gov/airnow/	Eastern US Ozone	Hourly
Meteorological	NOAA National Data Centers http://www.nndc.noaa.gov/	U.S. Surface Meteorology	~ Month time lag
	NOAA National Data Centers http://www.nndc.noaa.gov/	U.S. Visibility	~ Month time lag
	Air Resources Laboratory http://www.arl.noaa.gov/ready/etaanim.html	North American Modeled meteorological data	Two day Forecast
Satellite	SeaWiffs http://seawifs.gsfc.nasa.gov	N. American multi-channel Visible Imagery	Daily
	GOES-8 http://rsd.gsfc.nasa.gov/goes/	N. American multi-channel Visible and Infrared Imagery	Hourly
	TOMS http://jwocky.gsfc.nasa.gov/	N America TOMS Absorbing Aerosol Index-	Daily

Figure 2

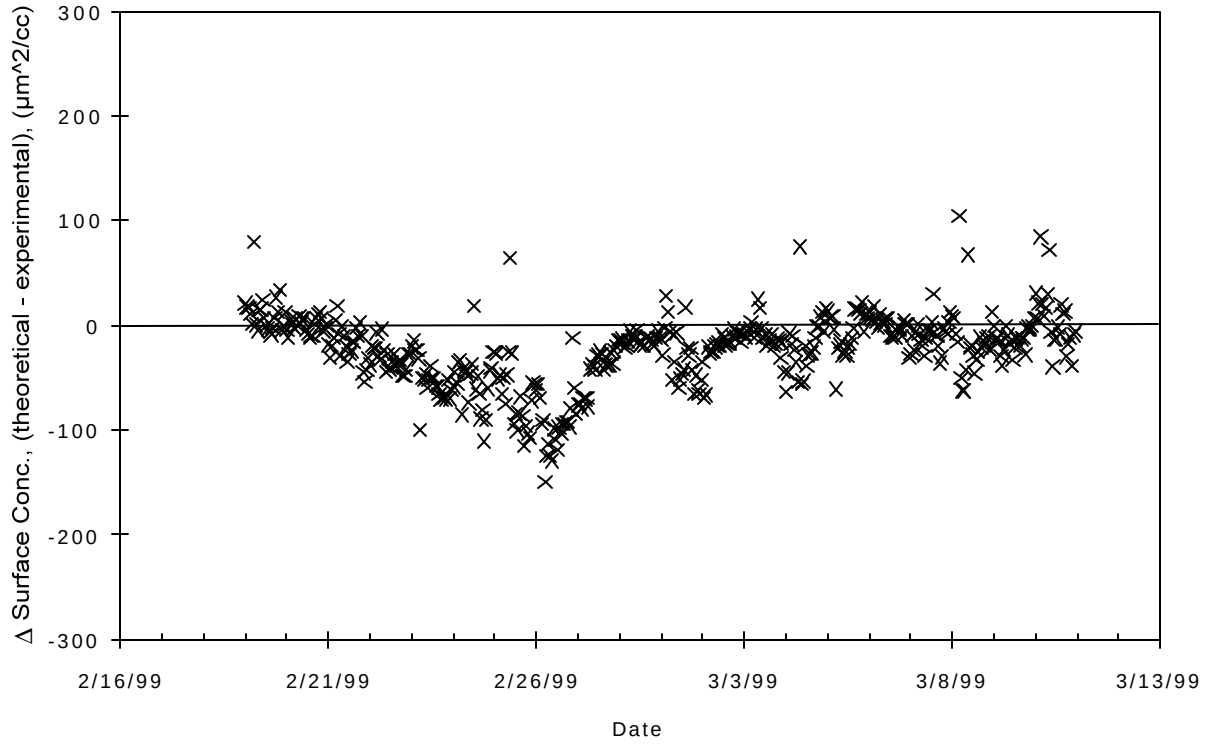
Figure 3

Figure 4

Figure 5



(a)



(b)

Figure 6. Surface areas obtained from measurements of size distributions ("theoretical") and from measurements of moments ("experimental"): (a) surface areas; and (b) difference in surface area between the two methods.

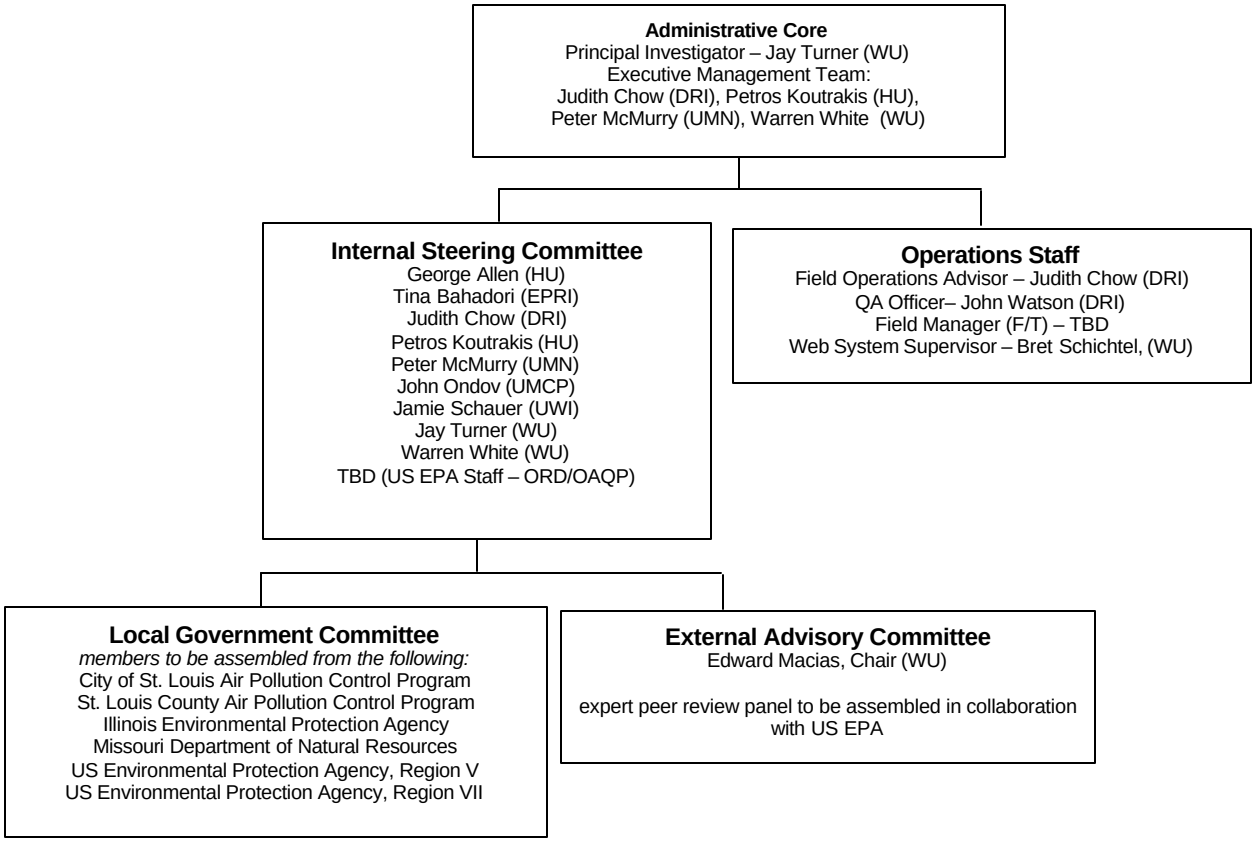


Figure 7. Organizational chart for the St. Louis Supersite program.

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I. QUALITY ASSURANCE NARRATIVE STATEMENT

A quality system for the proposed St. Louis Supersite project will be put in place that meets or exceeds the requirements of ANSI/ASQC E4. The details of the quality system will be specified in a Quality Assurance Project Plan (QAPP) that will be developed in accordance with U.S. EPA's R-5 "EPA Requirements for Quality Assurance Project Plans" and U.S. EPA's G-4 "Guidance for the Data Quality Objectives Process." QAPPs for complex projects, as proposed here, have been implemented in the past for projects conducted by investigators of the St. Louis Supersite Consortium. Examples of such QAPPs include, but are not limited to, Desert Research Institute's U.S. DOE sponsored Upper Ohio River Valley Characterization Study, and The Wisconsin State Laboratory of Hygiene's U.S. EPA sponsored Lake Michigan Tributary Study. Although the complete details of the St. Louis Supersite QAPP cannot be presented here, the underlying principles of the QAPP and an outline of the mechanism that will be put in place to assure the data quality are provided.

Through a process of continual improvement and in cooperation with the U.S. EPA and other partners, the proposed project will strive to not only meet, but exceed, the quality objectives of the expected users of our products. Throughout the study, emphasis will be placed on the technical accuracy of the work performed. This applies to the actual sampling, analytical work, modeling, and written and verbal reports. In order to maintain and develop personnel capabilities, people involved in the project will undergo continuing training. The project will also provide a work environment based on the integrity and professionalism of its staff. Such an environment will help ensure that the work is performed with a dedication to excellence and continuous improvement.

A quality assurance officer will be assigned from the existing Desert Research Institute (DRI) staff to be responsible for ensuring quality practices are carried out. One of the first tasks of the project will be to develop the QAPP. The plan developed will consist of the following chapters: (1) Project Description, (2) Project Organization and Responsibilities, (3) Quality Assurance Objectives including data quality objectives (DQOs) and measurement quality objectives (MQOs), (4) Site Selection and Sampling Procedures, (5) Sample Custody, (6) Calibration Frequency and Procedures, (7) Analytical Procedures, (8) Data Reduction, Validation and Reporting, (9) Internal QC Checks, (10) Performance and System Audits, (11) Preventive Maintenance, (12) Calculation of Data Quality Indicators, (13) Corrective Actions, and (14) Quality Control Reports. The nine items listed in the proposal instructions will all be handled in accordance with established quality control procedures. Acceptance criteria, sampling design, sample handling and custody, methodology, performance evaluation, data reduction and reporting criteria, and data use objectives will be explicitly addressed in the quality assurance plan. A draft QAPP will be forwarded to U.S. EPA for review six months prior to commencing measurements, with a final QAPP (which responds to U.S. EPA comments) to be forwarded to U.S. EPA and all project Principal Investigators two months prior to commencing measurements.

The quality goal of the St. Louis Supersite is to meet or exceed all of the data requirements of the end users who ultimately will utilize the data generated by the project. This goal will be

achieved through the implementation of robust systems for instrument calibrations, system audits, performance audits, and on-site performance tests. These procedures will be implemented for all measurements performed directly or indirectly by the St. Louis Supersite. The proposed measurements are described in the main body of the proposal and are summarized in Table 4 (Attachment D-I).

Every measurement consists of a value, a precision, an accuracy, and a validity. Quality Control (QC) and quality auditing establish the precision, accuracy, and validity of measured values. Quality Assurance (QA) integrates quality control and quality auditing to determine these four attributes of each environmental measurement. QC is the responsibility of each investigator. QC prevents, identifies, corrects, and defines the consequences of deviations that might affect the precision and accuracy, and/or validity of the measurements. QA makes certain that QC activities are being carried out, evaluates accuracy against independent and traceable standards, acquires the information generated by QA activities, defines how the measurement attributes are determined and reported, and creates data qualification statements for data analysts.

The Quality Assurance Project Plan (QAPP) will be supported by detailed Standard Operating Procedures (SOPs) describing each measurement procedure (U.S. EPA, 1995). SOPs include: (1) summary of measurement method, principles, expected accuracy and precision, and the assumptions for validity; (2) materials, equipment, reagents, and suppliers; (3) individuals responsible for performing each part of the procedure; (4) traceability path, primary standards or reference materials, tolerances for transfer standards, and schedule for transfer standard verification; (5) start-up, routine, and shut-down operating procedures and an abbreviated checklist; (6) data forms; (7) routine maintenance schedules, maintenance procedures, and troubleshooting tips; (8) internal calibration and performance testing procedures and schedules; (9) external performance auditing schedules; and (10) references to relevant literature and related SOPs.

Quarterly project progress reports will be forwarded to U.S. EPA (Table 9). These reports will include a section addressing how the quality assurance requirements are being met with emphasis on the assurance of data quality relevant to measurements and data generation. A Quality Assurance Final Report (QAFR) will be provided to U.S. EPA at the end of the project that summarizes the extent to which DQOs and MQOs were met. This QAFR will be included as an appendix to the project final report.

Activities to be Performed

The study objectives are stated in Section D.1. Data analysis activities are detailed in Section D.2.3. Measurement activities are described in Section D.2. Simultaneous health studies are specified in section D.1.2.

QA activities include: (1) assembling, reviewing, and archiving SOPs; (2) summarizing QC and QA procedures with measurement descriptions in a QAPP; (3) specifying primary, calibration, performance test, and audit standards; (4) specifying data reporting conventions; (5) conducting systems audits of field, laboratory, and data management systems; (6) conducting performance audits of field and laboratories; and (7) preparing data qualification statements.

Several of the methods described in Table 4, especially those for gases and meteorological measurements, are well-established with commonly available transfer standards for calibration and auditing. Many of the *in situ* measurements systems are being used for the first time in a long-term program and their reliability is not proven under these conditions. It is desired to have >95% data recovery with precisions <±10% for values exceeding ten times lower quantifiable limits. The goal for accuracy, as determined by comparison with independent traceable standards, is to be within a single standard deviation of precision for each measurement. These goals have been achieved in previous studies for in situ gas monitoring, filter sampling/laboratory analysis of elements and ions, and for meteorological observables. Particulate carbon and organic sampling and analysis methods have not shown as good accuracy and precision; standards and methods to establish these measurement attributes need to be developed as part of this project. Although continuous particle size measurements have been taken in special studies, practical methods to evaluate their performance in long-term studies are still lacking, as are quantitative estimates of their accuracy and precision.

The Quality Assurance Manager will establish methods to quantify accuracy, precision and validity for each piece of data entered into the project data base. These attributes will be evaluated to produce a data qualification statement related to each data analysis activity. The statement will include data completeness, values above lower quantifiable limits, relative precision as a function of concentration, accuracy as determined by performance audits, and frequencies of data validation flags. It will also review current literature, and comparisons made in this study, to evaluate the response of different measurements systems to changes in environmental variables and aerosol composition. The data qualification statement will define the level of signal in an environmental cause that is needed to exceed the noise of the measurements system; it will be used by data analysts to evaluate the extent to which sought relationships are real or are an artifact of the measurement process.

Study Design

Section D.1.1 described previous work performed in the St. Louis area that was examined in selecting the monitoring locations and times. Ongoing and planned health studies that complement Supersite measurements were described in Section D.1.2. The St. Louis airshed is affected by heavy industry that is not as proximate to many other monitoring sites in the U.S. and provides an opportunity to evaluate heavy metal and organic aerosol components that are not anticipated at other locations. Section D.2.1 and D.2.2 presented the measurements and samples to be collected. Selection of satellite site locations will be completed prior to submitting the QAPP, which will address siting criteria and other issues of representativeness.

Sample Handling and Custody Procedures

Sample handling, chain of custody, and archiving are specifically treated in SOPs. Most of the measurements specified in Table 4 are in situ, with instruments located in environmentally controlled shelters. However, electronic data files acquired in the field will be handled with well defined sample handling and sample custody procedures to assure high quality data. To minimize sampling losses or changes and to promote comparability among these instruments: (1) sample inlet lines will be as short as possible by locating instruments close to the shelter

ceiling; (2) inlets will be at a common height above rooftop level (~1.5 m), equivalent to the height of FRM inlets; (3) sample lines will be made of conducting material with straight or gently curving entries to instruments to minimize particle losses; (4) sample line diameters will be as small as possible to minimize residence time that might causes changes in temperature and humidity.

Sample substrates and samples will be prepared in clean laboratories and shipped to and from the field by overnight transport in cooled (<4°C) containers containing temperature indicators as required. Samples will be stored in on-site refrigerators before and after sampling. Shipments will be coordinated between the field and laboratories to assure that they are met upon arrival and stored according to procedures. Sample identifiers will be bar-coded to indicate sample type, analysis laboratory, and sampling time and location. These identifiers will be entered into field and laboratory data acquisition systems to track sample status at any time during the project. The QA Manager will review chain of custody processes and data throughout the project and recommend corrective actions.

Sample Analysis Methods

Table 4 identifies the sampling and analysis methods and Section D.2.2 describes how these methods will be applied to Supersite measurements. Several common quality control activities will take place for all analyses: (1) acceptance testing for contamination of substrates, reagents, extraction vials prior to use; (2) field and laboratory blank designation and analysis to determine blank levels and variability; (3) periodic performance tests of zero and span values for field and laboratory instruments to determine reproducibility and calibration drift; (4) periodic multi-point calibrations in the range of ambient concentrations to determine linearity and concentration relationships; and (5) data validation flags for field and laboratory operations that indicate deviations from procedures. Records of results from these common quality control activities will be compiled into a separate data base by the Quality Assurance Manager and used to develop the data qualifications statement to be included in the QAFR.

Calibration and Performance Evaluation Procedures

Several types of standards are needed for calibration, auditing, and performance tests. Primary standards are well characterized, protected, with stable concentrations to which all other standards are traceable. Transfer standards are often more easily produced or commonly available and are traceable to primary standards. These are used for calibration, performance testing, and auditing. The same standards can be used for calibration and performance testing, but audit standards should be independently traceable to primary standards. Depending on how practical they are to use, performance standards may consist of a substitute that measures instrument electronic response rather than response to a specific value of an observable. Table 10 (Attachment D-I) identifies primary and transfer standards and the frequency of application for calibration, performance testing, and auditing. Methods for presenting these standards to instruments depend on the instrument audited. Flow rates are relatively simple to evaluate, while continuous monitor response to particle size is impractical to evaluate in great detail under field conditions.

The University of Minnesota Particle Technology Laboratory's aerosol generation and measurement systems will be used as the primary standards for particle size measurements because these standards are not available elsewhere. Laboratory calibration determines instrument response to particles of known size, composition, and concentration that have been generated for several decades at UM. Differential Mobility Analyzers (DMA) (Liu and Pui, 1974) generate monodisperse calibration aerosols in the 3 nm to 1 µm diameter range with removal of multiply charged particles in the upper end of this range (Romay-Novas and Pui, 1988; Gupta and McMurry, 1989). The size of the classified particles depends on flow rates, classifying voltage and geometrical factors (Knutson and Whitby, 1975), as confirmed by electron microscopic measurements at NIST as part of a 0.1 µm Standard Reference Method for sizing 0.1 µm particles (Kinney et al., 1991). Particles produced with a DMA typically vary by ±10% about a mean size that is accurate to within 5%.

A Vibrating Orifice Aerosol Generator (VOAG) (Berglund and Liu, 1973) generates monodisperse spherical droplets in the 1 µm to 10 µm diameter range from an oleic acid in ethanol solution. Particle size is determined by flow rate of the liquid through the vibrating orifice, vibration frequency of the orifice, and the concentration of nonvolatile solute in the liquid solution flowing through the orifice. Microscopic confirmation (Berglund and Liu, 1973) has shown that particles generated with this instrument are uniform to within 1.4% and are routinely within 2% of the expected size.

Particles generated by these instruments are presented to the field instruments and simultaneously monitored by a laboratory Condensation Particle Counter (CPC) and an aerosol electrometer. CPC counting efficiencies are close to 100% (Stolzenburg and McMurry, 1991; Zhang and Liu, 1991) for the size ranges and concentrations expected at the St. Louis Supersite. At least 1000 particles for each measurement are counted so that statistical counting errors are <3% (square root of count number). Aerosol electrometer uncertainties (Liu and Pui, 1974) depend on signal-to-noise, which is determined by aerosol concentration. Laboratory concentrations are generated at concentrations with signal-to-noise levels ~100, resulting in calibration biases of <2%.

Pressures that affect particle classification by the DMA are monitored with MKS Barotron pressure gauges that are accurate to ±0.5% of full scale. For the pressures that will be encountered in St. Louis, the maximum error in pressure measurement is ±5%.

Calibration, performance testing, and auditing methods for laboratory operations are largely based on the preparation of standard solutions from mineral salts. The National Institute of Standards and Technology (NIST) does not provide these types of standards. Standard solutions in a large range of concentrations are available commercially for inorganic monoatomic and polyatomic ions. This is not the case for organic compounds; not all of the species specified in Section D.2 are available. Multi-element standards will be prepared for calibration and audit for as many species as are practical, although the exact composition will depend on the extraction, derivitization, and injection procedures that are developed for these samples.

Gas and meterological monitors are often used in compliance networks, as common procedures and standards have been developed for their calibration and auditing. Some of the novel

measurements in Table 10 will be evaluated by comparison with other measurements that have traceable standards and audit trails.

The Quality Assurance Manager will conduct a systems audit at each monitoring site and at each laboratory, a performance audit and/or intercomparison for each laboratory procedure, and three field performance audits. Systems audits examine all phases of measurement and data processing activity to determine that the procedures are being followed and the operational people are properly trained. The systems audit is intended to be a cooperative assessment resulting in improved data, rather than a judgmental activity. Performance audits establish the extent to which data specifications are being achieved in practice and evaluate measurement accuracy against independent standards. The field systems audit will be conducted near the beginning of the project after all equipment is installed and operating. It will be followed by the first field performance audit. These audits will identify deficiencies and implement corrective actions. Subsequent field performance audit results will be used to define the accuracy of field measurements.

Laboratory audits will consist of presentation of standards with known concentrations to each laboratory. These will be analyzed according to normal procedures and the results will be compared with the standard values. As shown in Table 10, reliable transfer standards can be obtained for mass, elements, ions, and total carbon. Common standards are not available for organic and elemental carbon. Standards can be prepared for some, but not all, of the organic compounds.

Inter-laboratory comparisons will operate on the exchange of portions of the same filters or sample extract. Mass, elemental, ion, and carbon analysis can all be performed on portions of the same filter. For elemental analysis, non-destructive XRF will be applied prior to destructive methods such as ICPMS, INAA, and GFAAZ. Since the entire sample must be extracted for organic speciation, extract residues will be analyzed at the DRI laboratory for comparison with analyses from the UWI laboratory.

Data Reduction and Reporting Procedures

The data management system will consist of a set of inter-related files with referential integrity in Microsoft Access. The following types of tables will be included in the project database:

- **Measurement locations:** Each measurement location is identified with a unique alphanumeric site ID accompanied by its name and address, coordinates, elevation, its primary operator, and a summary of measurements taken at the site for different monitoring periods. Coordinates are determined with GPS using map basis NAD-83 (Federal Aviation Administration convention). The GPS time stamp is recorded to correct coordinate deviations.
- **Variable definitions:** Each variable is assigned a unique code that is accompanied by its definition, units, averaging time, applicable temperature and pressure adjustments, and data reporting format.
- **Data validation flags:** Flags specific to each measurement investigator are translated into a common set of validation flags that are carried with each data point. These are currently

being defined by EPA for its speciation program, and this will be a starting point for St. Louis Supersite data validation flags.

- **Data tables:** Basic data tables are constructed in normalized formats that have the same structure for different types of data. Each record contains the site code, sample date (MM/DD/YYYY), sample time (HH:MM:SS, CST), variable code, measurement value, measurement precision, validity code, and validation level. These files will be transparent to most users and can be easily manipulated into convenient data analysis forms. Missing or invalid measurements will contain a "NULL" value. Modern data management software permits this in place of the –99 previously used. Separate tables are produced for different averaging times and for non-uniform data sets.
- **Validation tables:** These tables contain detailed information on specific samples indicating the nature of the data qualification. These tables also contain the validation level assigned to each data item.

Data validity levels are designated in the validation tables at different stages in the data acquisition process. Level 0 designates data sets downloaded from a field instrument that have not been examined. These measurements are used to evaluate instrument performance and possibly to select periods for chemical speciation. They are not used for interpretive purposes. Level 1 data has been evaluated by the measurement investigator prior to submission to the data base. Values are removed for instrument downtime and performance tests, adjustments for calibration deviations are applied, extreme values are investigated, internal comparisons are made, blanks are subtracted, precisions are estimated and propagated, and appropriate data qualification flags are assigned. These are submitted to the data base manager who applies several additional tests. For sequential measurements, jump tests, standard deviation tests, and extreme value tests often identify values that need to be investigated. Level 2 data has completed intercomparison tests between data sets. These tests often result in the investigation of several samples that do not follow the same pattern as other measurements. These are investigated, sometimes re-analyzed, and re-designated as valid, invalid, or suspect as a result of the investigation.

Level 3 validation occurs after measurements are used to test hypotheses and values that are found contradictory to other values have been investigated. The quality of these measurements is especially important as they often indicate large deviations from conventional wisdom that should not be confused with measurement error. The first assumption upon finding a measurement inconsistent with physical expectations is that the unusual value is due to a measurement error. If, upon tracing the path of the measurement, nothing unusual is found, the value can be assumed to be a valid result of an environmental cause. Unusual values are identified during the data interpretation process as the following: 1) extreme values; 2) values that would normally track the values of other variables in a time series; and 3) values for observables that would normally follow a qualitatively predictable spatial or temporal pattern. The Quality Assurance Manager will audit the integrity of the data base by randomly selecting data sets submitted by each investigator and tracing it through the data management system to its final value in the finished data base. Unit conversion, sample times, site and variable codes, and

data validation flags will be applied manually, and the results will be compared with data extracted from the web-based data set available to all investigators.

Intended Uses of the Data

Data analysis activities are described in Section D.2.3. For quality assurance purposes, substantial comparisons among measurements will be made to determine their predictability, comparability, and equivalence. Although the different observables measured are quite diverse, it is possible that they may be highly correlated owing to their quantification of related particle properties or to large fluctuations caused by emissions and meteorology. Relationships between variables will depend on the composition of the aerosol as well as meteorological conditions. The QA Manager will apply measures of predictability, comparability, and equivalence to data sets stratified by aerosol composition, and season. Predictability requires a consistent and reliable relationship between measurements, even if they are of different quantities. Light scattering or light absorption measurements are examples of continuously measured particle properties from which $PM_{2.5}$ concentrations might be predicted. Comparability can be established between monitors that ostensibly measure the same observable, but with different principles. CAMMS, FRM, and HEADS measures of $PM_{2.5}$ mass are expected to be comparable, and if they are shown to be so they can be used interchangeably in data analysis. Equivalence is a regulatory term that allows a method to be designated as Federal Equivalent Method (FEM) that can be used to determine compliance. Equivalence is more demanding than predictability or comparability in that it requires demonstration of comparability within high tolerances over a wide range of concentration loadings and measurement environments. Several empirical and statistical measures will be applied to evaluate predictability and equivalence (Mathai et al., 1990). Linear regression is most commonly used and is the requirement for FEM relationships with FRMs. Regression slopes and intercepts with effective variance weighting (Watson et al., 1984) for each set of paired measurements are evaluated with their standard errors. The effective variance weighting includes the precisions of both variables in the calculation and bases the standard errors on them. When the slope equals unity within three standard errors, when the intercept does not significantly differ from zero within three standard errors, and when the correlation coefficient also exceeds 0.9, the measurements are considered comparable. When the correlation coefficient exceeds 0.9 but the slope and intercept criteria are not met, the dependent variable is predictable from the independent variable. Other comparison measures include average ratios and standard deviations, ratios of averages, and the distribution differences (X minus Y) for $<1\sigma$, 1σ to 2σ, 2σ to 3σ, and $>3\sigma$ precision intervals. These measures indicate the extent to which long-term averages are more or less equivalent than individual values and whether or not the majority of differences are within stated uncertainty intervals.

Procedures to Evaluate Success of Project

Success of the project will be evaluated in terms of: (1) accuracy, precision, validity, and completeness of acquired data; (2) extent to which data can be used to meet the stated project objectives; (3) confidence of conclusions regarding any hypotheses; (4) consistency of St. Louis Supersite measurements with those at other Supersites; (5) integration with other monitoring

networks and research studies; (6) leveraging of Supersite resources with those from other agencies; and (7) relevance of study conclusions to Supersite program objectives.

A Quality Assurance Final Report (QAFR) by the Quality Assurance Manager will discuss accomplishments with respect to each of these areas. The first topic will be assessed by the data qualification statement described above. The second topic will be assessed by the data analysts as they use the acquired measurements to test various hypotheses. Part of the success in using the data will be the ratio of data manipulation versus data analysis time. The web-based data delivery system must allow all analysts to quickly integrate measurements most convenient for their tasks. Data quality information must be quickly available for consultation when inconsistencies with conceptual models are found.

Confidence in study conclusions will be evaluated by each investigator according to the following criteria: (1) high confidence when there is low uncertainty in the data or data analysis approach or the conclusion is supported by more than one independent analysis approach, each of which has moderate uncertainties; (2) medium confidence when there is moderate uncertainty in the data or data analysis approach and independent analysis approaches were not applied; and (3) low confidence when there is large uncertainty in the data or data analysis approach and independent analysis approaches were not applied or were contradictory. These ratings were applied by each investigator and modified under scrutiny by all investigators in the Northern Front Range Air Quality Study (Watson et al., 1998). Decision-makers found it useful for scientists to express their own levels of belief in the outcome of their study.

Consistency of St. Louis measurements with those from other Supersites will be included in the data qualification statement. This will include a table of overlapping measurements acquired at the different sites that will facilitate generalization of St. Louis conclusions to those of other locations. Substantial integration with other monitoring networks and research studies, as well as leveraging opportunities, have been identified in Section D. The extent to which these opportunities are realized will be evident in the project reports and publications. These reports and publications will be judged by the project sponsors concerning their relevance to Supersite objectives.

External and Peer Review

Section D.2.5 summarizes the External Advisory Committee and Local Government Committee which will be convened to review the QAPP and other project plans and provide recommendations on how data quality might be enhanced, the extent to which Supersite measurements can be used for planning purposes and health studies, and evaluation of study findings. The External Advisory Committee will draw members from the following: (1) principal investigators for concurrent health studies; (2) EPA headquarters representatives; and (3) other project sponsors. The Local Government Committee will include officials from state and local air quality planning agencies.

Scientific papers will be submitted to external peer review by each investigator and the resulting comments will be addressed in finally published papers.

The Principal Investigator and selected task investigators will report on progress and results at periodic meetings of Supersite investigators. These presentations will be structured to obtain feedback and experience from similar projects taking place in other U.S. cities.

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